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Final Report
May 17, 1976, to February 16, 1977

DENSITY ESTIMATION FOR NEW SOLID AND LIQUID EXPLOSIVES

By: Craig M. Tarver, Clifford L. Coon and John M. Guimont

Prepared for:

NAVAL SURFACE WEAPONS CENTER
White Oak Laboratory
Silver Spring, MD 20910

Attention: Mr. Charles Dickinson

Contract No. N60921-C-0146
SRI Project PYU 5425

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PREFACE

This report is submitted in partial fulfillment of the contractual obligation for Contract No. N60921-76-C-0146 entitled, "Density Estimation for New Solid and Liquid Explosives." The report contains a summary of work performed during the period May 17, 1976, through January 16, 1977.

The research program was performed by staff of SRI's Physical Sciences Division under the supervision of M. E. Hill and Donald L. Ross. Craig M. Tarver and Clifford L. Coon were the principal investigators. Other personnel who participated in the research include John M. Guimont, Gerald E. Manser, Robert L. Simon, and D. V. H. Son.

We wish to acknowledge the valuable suggestions and discussions given to this project by Dr. M. J. Kamlet, Project Monitor, and Dr. Horst G. Adolph of Naval Surface Weapons Center.

REPORT HIGHLIGHTS

The group additivity approach to estimating density was studied and shown to be reasonably accurate. The densities of approximately 180 explosives were estimated. Where direct comparison was possible, 37% of the values were accurate within 1% and 70% were accurate within 2%. Concurrently, the synthesis of energetic oxidizers was investigated

SUMMARY

The group additivity approach was shown to be applicable to density estimation. The densities of approximately 180 explosives and related compounds of very diverse compositions were estimated, and almost all the estimates were quite reasonable. Of the 168 compounds for which direct comparisons could be made (see Table 6), 36.9% of the estimated densities were within 2-3%, 8.9% were within 3-4%, and 9.0% were more than 4% different from the measured densities. Thus, of the densities estimated in this study, 82% were within 3% of the measured density. The average absolute error in density was approximately 0.022 g/cm³, and the absolute error in density exceeded 0.04 g/cm³ for only 24 of the 168 compounds (14.3%). The largest errors occurred for compounds with several bulky, highly polar groups in close proximity, and for compounds containing groups whose calculated molar volumes were based on density data for only two or three compounds. As more density data for a certain group configuration become available, the molar volume can be determined more accurately, and the overall agreement between measured and estimated densities of compounds containing that group should improve.

Synthetic work was carried out on a number of newly postulated explosives or explosives whose syntheses were expected to be difficult. Progress was made toward the synthesis of 3,6-bis(nitrimino)-3,6-dihydro-1,3,4,5-tetrazine and 3,5-bis(nitrimino)- Δ' -2,3,4-triazoline, which contain no hydrogen and are highly energetic. Syntheses were developed for the preparation of the important intermediates hexachloroazobisformamidine and 3,5-bis(chlorimino)- Δ' -1,2,4-triazoline. In addition, the oxidation of diaminotetrazine was partially successful in that the partially oxidized intermediate, 3-amino-6-hydroxylamino-s-tetrazine, was isolated.

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I DENSITY ESTIMATION

Introduction

Discussions at the ARPA Workshop on Advanced Warhead Technology (San Diego, 1974) and at the Naval Sea Systems Command Program Review meeting (Asilomar, 1974) showed the urgent need to rapidly and inexpensively assess and surpass the massive Russian effort to synthesize new explosives. The Naval Surface Weapons Center (NSWC), White Oak, is surveying the Russian literature on the development of new explosives. As new families of explosive compounds are identified, their detonation properties must be calculated to determine the compounds that offer advantages over explosives currently in use and that should therefore be synthesized.

The main detonation property that determines the impulse delivered by the explosive is the Chapman-Jouguet (CJ) pressure, P_{CJ} , which is given by:

$$P_{CJ} = \frac{\rho_0 D^2}{K + 1}, \quad (1)$$

where ρ_0 is the initial density of the explosive, D is the detonation velocity, and K is the adiabatic expansion coefficient of the chemical reaction product gases at the CJ state. Measurements of P_{CJ} for various explosives have shown that P_{CJ} is proportional to the square of the initial density. Therefore, to develop more powerful explosives, energetic molecules with very high densities must be identified.

The CJ pressure of an explosive can be calculated to within experimental measurement accuracy by a thermodynamic equilibrium computer code, such as SRI's TIGER code,^{1*} or, for explosives containing only

* References are presented at the end of Section I

C, H, O, and N atoms, by the empirical formula of Kamlet et al.² These methods require only the molecular formula, the heat of formation, and the initial density of the explosive as input data for a CJ detonation calculation. The group additivity approach to heat of formation estimation^{3,4} is usually accurate to within ± 2 kcal/mol; and, since explosives release 200-500 kcal/mol of energy when detonated, this approach may be confidently used in detonation calculations for hypothetical explosive molecules. Reliable detonation calculations thus require only an accurate method of estimating densities of explosives. One major objective of this research program was to develop such a method.

The prediction of the density of a solid or liquid explosive with no knowledge of its physical properties is difficult; no general method to predict the density of complex organic molecules exists. Before this program began, three general approaches to density prediction were reviewed: potential function, the theory of close packing for solids, and group additivity. The potential function approach is attractive because it evolves from first principles, and some recent progress⁵ has been made in its application to large organic molecules. However, as shown by Lee et al.,⁶ the potential function approach is mainly concerned with minimizing the potential energies for an arbitrary set of potential functions and then calculating the resulting interaction energies. Density estimates obtained as a secondary feature of the approach are usually inaccurate,⁶ and development of an accurate potential function approach to density prediction would be very expensive and time-consuming.

For solid organic molecules, a great amount of crystallographic data has been generated and summarized by Kitagorodskii.^{7,8} A theory of close packing has been developed to explain the measured densities of solid crystals. However, this crude theory relies on experimentally measured packing coefficients for each molecule. Although several groups

are working on the problem,⁹ no theoretical explanation of the measured packing coefficients exists. Therefore the crystallographic close packing approach is not sufficiently developed to use as a tool for predicting densities of solid explosives.

The group additivity approach to density prediction was used by Exner¹⁰ to estimate the densities of 870 organic liquids. He determined the densities of very simple liquids to within a standard deviation of 0.003g/cm^3 . For liquids comparable in complexity to most liquid explosives, he determined the densities to within a standard deviation of 0.008 g/cm^3 . Exner concludes that the group additivity approach is invalid only for liquids with extremely branched chains or directly bonded functional groups.

No corresponding study of solid compounds by the group additivity approach has been previously reported. The greater degree of internal ordering and the possible existence of more than one stable polymorphic form make density prediction more difficult in solids. However, because group additivity works well for liquids and because the other two approaches cannot be easily developed, the group additivity approach was used in this study for density prediction in both solid and liquid explosives.

The resulting density estimations for approximately 180 known explosives and related compounds and for some of the new explosives synthesized during this research program are reported in the "Results" portion of this section. Discussion of these results and recommendations for future work complete this section.

Results

Because the main objective of this research effort was to determine the general usefulness of the group additivity approach in predicting explosive densities, an effort was made to calculate group values and predict densities for the maximum possible number of explosives and

related compounds. For group additivity to be a worthwhile tool in predicting densities of new explosives, it must be applicable to all types of organic explosives: aromatic, aliphatic, alicyclic, and heterocyclic. Therefore density data on these types of compounds were collected from several handbooks.¹¹⁻¹⁵ In most cases, density data found in two or more sources were in reasonable agreement; but for some compounds, two conflicting density values or only one value from an older, less reliable source was obtained. Thus some of the measured densities used for comparison in this report may be incorrect and may result in poor correlations with the estimated densities.

When the available density data for a series of explosives were assembled, the groups present in each compound were identified and a linear equation was written in terms of molar volume for each compound. A simple computer program was used to calculate the group molar volume contributions that produced the minimum total absolute error in molar volume for that particular set of compounds. Most of the calculated group values are based on data from 10-20 compounds and are considered to be reliable, but some of the calculated values for the less common groups are based on only two or three densities and thus are not as reliable. In this first-generation group additivity approach, only one value of the molar volume is assigned to each group, regardless of where it appears in the molecule. No second-order effects, such as nearest-neighbor interactions, phase changes, and crystalline structure changes, are considered when calculating these group values. A discussion of the possibility of including second-order effects in a more sophisticated group additivity approach, similar to the detailed models developed by Benson et al.³ for the estimation of various thermochemical properties, is presented in "Conclusions and Recommendations" at the end of this section.

The first explosives to which the group additivity approach was applied are 25 solid aromatic compounds containing NO_2 , OH , CH_3 , and NH_2 groups bonded directly to the benzene ring. Only five group values (Ca-H , Ca-NO_2 , Ca-OH , Ca-CH_3 , and Ca-NH_2 , where Ca designates an aromatic carbon atom) are required to describe these compounds. The group molar volumes that give the best overall agreement and the resulting density estimations are shown in Table 1.* The average error in Table 1 is 1.29%, which represents 0.022 g/cm^3 based on an average density of 1.692 g/cm^3 . The estimated density is within 1% of the reported density for 11 compounds, within 1-2% for 9 compounds, and within 2-3.3% for the other 5 compounds.

The use of only one molar volume for each group does not allow for density differences between isomers. For example, in terms of formulating high-density molecules, it appears to be much more favorable to have nitro groups para to each other rather than ortho or meta. This explains the significantly higher densities of p-dinitrobenzene and 1,2,4-trinitrobenzene relative to m-dinitrobenzene and 1,3,5-trinitrobenzene, respectively. There also appears to be a smaller advantage in placing nitro groups meta rather than ortho to reduce steric hinderance. Quantifying such effects for all possible nearest-neighbor interactions would result in a slightly improved overall agreement but would greatly increase the number of group values to be determined. The good overall agreement between measured densities and those calculated by using only one molar volume per group led to the use of this technique in predicting densities of explosives bound in other configurations.

The second major series of explosives and related compounds consists of 77 aliphatic compounds containing NO_2 , OH , F , CO_2H , and ONO_2 groups. Table 2 lists the calculated molar volumes for the 26 group configurations

* Tables are presented at the end of this section.

found in these compounds. Most of the group values are determined by comparing densities of 10-20 compounds containing that group, but nine of the group values (denoted by the letters f, m, q, r, s, t, u, v, and y in Table 2) are determined from density data on only two or three compounds and are considered to be less reliable. In the case of C-C, H₂, ONO₂ groups, two molar volumes are used. One value is used for nitrate esters similar to PETN in which three or four C-C, H₂, ONO₂ groups are bonded to a central carbon atom; another molar volume is used for nitrate esters like nitroglycerine (NG) that have C-C, H₂, ONO₂ groups bonded to separate carbon atoms.

The resulting density estimations of these 77 aliphatic compounds are shown in Table 3. Direct comparisons between the measured and calculated densities can be made for 71 of the 77 compounds. The average error is 1.70%, which represents 0.022 g/cm³ based on the average density of 1.294 g/cm³. Of the estimated densities, 48% are within 1% of the measured densities and another 28% are within 1-2% of the measured densities. Large errors occur for compounds with bulky or highly polar groups bonded in close proximity, such as oxalic acid and malonic acid. In the previously mentioned statistical study of density estimation by group additivity in liquids, Exner¹⁰ concluded that the approach is least accurate for highly branched chains containing several polar groups. This problem appears to be a real limitation of the group additivity approach in its present form, but it exists for only a small number of potential explosives. Second-order effects must definitely be considered to improve the density estimations for these explosives.

Many other existing and potential explosives are derivatives of amino, alicyclic, and heterocyclic compounds. Table 4 lists the calculated molar volumes for the 48 group configurations required to describe the 83 amines, nitramines, and cyclic compounds whose density estimations are tabulated in Table 5. Because nearly all the cyclic

compounds considered contain a 5- or 6-membered ring, the group values with a subscript c in Table 4 are derived from the available density data on alicyclic and heterocyclic compounds containing 5- or 6-membered rings. In general, the cyclic group molar volumes are a few cm^3/mol larger than the corresponding aliphatic groups. In the case of the C-C, H_2 , N-NO_2 group (letter k in Table 4), the available density data suggest that the same molar volume can be used in both aliphatic and cyclic systems. The molar volumes of two groups found in 8-membered rings (labeled with the subscript c=8 in Table 4) had to be determined to estimate the density of HMX relative to RDX. The molar volume of the group $[\text{C-H}_2, (\text{N-NO}_2)_2]_{c=8}$ found in HMX was calculated by taking the value for the corresponding group in RDX, $[\text{C-H}_2, (\text{N-NO}_2)_2]_c$, and subtracting the difference between the groups $(\text{C-C}_2\text{H}_2)_{c=8}$, which was determined by the density of cyclooctane, and $(\text{C-C}_2\text{H}_2)_c$ for 5- and 6-membered rings. This simple difference between a 6- and an 8-membered ring explains most of the difference in the densities of RDX and HMX. The calculated densities differ by 0.07 g/cm^3 , the measured densities are 0.094 g/cm^3 apart.

Direct comparisons of the measured and estimated densities can be made for 72 of the 83 compounds listed in Table 5. The average error is 2.054%, which represents 0.0214 g/cm^3 based on an average density of 1.0403 g/cm^3 . Of the estimated densities, 24% are within 1% of the reported values, 38% are within 1-2%, and another 19% are within 2-3%. This overall agreement is quite reasonable when compared with the results in Tables 1 and 3 and when the diverse nature of the compounds in Table 5 is considered.

Undoubtedly there are other explosives and related compounds whose densities have been measured, but the 179 compounds in Tables 1, 3, and 5 represent those obtained during a fairly extensive review of the open literature. The group molar volumes listed in Tables 2 and 4 should cover most other existing compounds. The overall results of the density estimations by this first-generation group additivity approach for the

168 compounds whose estimated and measured densities can be compared are summarized in Table 6. Of the estimated densities, 70% are within 2% of the measured densities, with another 12% within 2-3%. These results and the conclusions that can be drawn from them are discussed more fully in "Conclusions and Recommendations" below.

Because the major part of this research program was a synthesis effort aimed at producing high-density potential explosives and then comparing their measured and estimated densities, the group additivity approach was used in Table 7 to estimate the densities of 11 compounds that were proposed targets of the synthesis program and one compound that was recently synthesized at SRI. Efforts to synthesize the proposed compounds are summarized in Section II.

Tetranitroglycoluril (TNGU), which has a known density of 2.03 g/cm^3 , was used to obtain the group molar volumes required for density estimations of compounds 4, 5, and 6 in Table 7. These group molar volumes are included in Table 4. Furan, which is compound 51 in Table 5, is the base compound for the first two compounds in Table 7. Compound 3 in Table 7, discovered at WOI, and recently rediscovered at SRI, has a measured density of 1.85 g/cm^3 .

Conclusions and Recommendations

The main conclusion regarding the applicability of the group additivity approach to density estimation is that the results are very promising. Approximately 180 explosives and related compounds of very diverse natures were considered in a first-generation group additivity approach, and almost all the estimated densities were within 1% of the measured densities, 33.3% were within 1-2%, 11.9% were within 2-3%, 8.9% were within 3-4%, and 9.0% were more than 4% different from the measured densities. A 3% error in the estimated density of an explosive that has an actual density of 1.7 g/cm^3 and a CJ pressure of 300 kbar would cause an error of

approximately 18 kbar in the estimated CJ pressure, because pressure varies as the square of the density. This 6% error is within the experimental error of present methods of measuring the CJ pressure.¹⁶ Therefore, an error of this magnitude would not affect a decision about the usefulness of a new explosive molecule based on a CJ pressure calculation. Of the densities estimated in this study, 82% were within 3% of the measured density and thus would yield realistic estimates of the CJ pressure. The average absolute errors in density were approximately 0.022 g/cm³ in Tables 1, 3, and 5 and may be a better indication of the accuracy of the group additivity approach than do the percent errors. The absolute error in density exceeded 0.04 g/cm³ for only 24 of the 168 compounds (14.3%). Therefore 85.7% of the estimated densities could be used with confidence in CJ calculations.

As mentioned previously, the largest errors occurred for compounds with several bulky, highly polar groups in close proximity and for compounds that contain groups whose calculated molar volumes were based on density data for only two or three compounds. As more density data become available for a certain group configuration, the molar volume can be determined more accurately and the overall agreement between measured and estimated densities of compounds containing that group improved. Therefore, it is very important to obtain as much density information as possible for a series of related compounds before deriving the group values.

From the results of Exner¹⁰ and of this study, it can be concluded that the group additivity approach estimates densities of liquids very accurately, except in a few cases of very highly branched, polar molecules. Group additivity is therefore a useful density estimation tool for the many liquid explosives that are known and those that will be synthesized. Inclusion of second-order effects, such as correction factors for nearest-neighbor interactions, should reduce the errors in density for the highly branched polar molecules.

The group additivity approach also worked well for solid explosives when the group values were determined from data on many similar compounds, such as the aromatic compounds in Table 1. Slight differences in the crystalline packing geometries of these compounds were effectively averaged over as the group molar volumes were determined. In compounds that are not as similar as the aromatic explosives and in compounds that have several stable polymorphic forms, the difference in crystal geometries could have significant effects on the actual density. The first-generation group additivity approach used in this study cannot predict these density changes. However, inclusion of second-order corrections for the various possible crystal configurations may allow group additivity to successfully predict different densities for various polymorphs of a solid explosive.

Based on the accuracy of the group additivity approach in predicting densities of liquid and solid explosives, and based on the need for a reliable approach to density estimation for hypothetical explosive molecules, it is recommended that the group additivity approach be extended to include second-order corrections for phase changes, nearest-neighbor interactions, effects of crystal geometry, and other factors. Together with a CJ calculation technique and a related synthesis program, an expanded group additivity approach would constitute a rapid and inexpensive method for selection of more powerful candidate explosives.

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Table I
DENSITY ESTIMATIONS FOR 25 KNOWN SOLID AROMATIC EXPLOSIVES CONTAINING NO_2 , OH, CH_3 , AND NH_2 GROUPS

Explosive	Molecular Weight	Measured Density (g/cm ³)	Groups Present	Calculated Molar Volume (cm ³ /mol)		Calculated Density (g/cm ³)	% Error
				Calculated Molar Volume (cm ³ /mol)	Calculated Density (g/cm ³)		
-Ca=NO ₂	29.697	16.019	-Ca-OH	16.019	1.692	16.019	0.447
-Ca-H	11.876	25.963	-Ca-CH ₃	25.963	1.286	25.963	0.190
		15.063	-Ca-NH ₂	15.063	1.286	15.063	0.190
o-Dinitrobenzene	168.11	1.565	4(Ca-H)+2(Ca-NO ₂)	106.90	1.572	1.572	0.447
m-Dinitrobenzene	168.11	1.575	4(Ca-H)+2(Ca-NO ₂)	106.90	1.572	1.572	0.190
p-Dinitrobenzene	168.11	1.625	4(Ca-H)+2(Ca-NO ₂)	106.90	1.572	1.572	3.262
1,3,5-Trinitrobenzene	213.11	1.688	3(Ca-H)+3(Ca-NO ₂)	124.72	1.769	1.769	1.214
1,2,4-Trinitrobenzene	213.11	1.73	3(Ca-H)+3(Ca-NO ₂)	124.72	1.769	1.769	1.214
Hexanitrobenzene	348.10	1.988	6(Ca-NO ₂)	178.18	1.951	1.951	1.710
3,5-Dinitrophenol	184.11	1.702	3(Ca-H)+2(Ca-NO ₂)+2(Ca-OH)	111.04	1.658	1.658	2.565
2,3-Dinitrophenol	184.11	1.681	3(Ca-H)+2(Ca-NO ₂)+2(Ca-OH)	111.04	1.658	1.658	1.368
2,4-Dinitrophenol	184.11	1.683	3(Ca-H)+2(Ca-NO ₂)+2(Ca-OH)	111.04	1.658	1.658	1.485
3,4-Dinitrophenol	184.11	1.672	3(Ca-H)+2(Ca-NO ₂)+2(Ca-OH)	111.04	1.658	1.658	0.837
Picric acid	229.10	1.763	2(Ca-H)+3(Ca-NO ₂)+2(Ca-OH)	128.86	1.778	1.778	0.831
Styphnic acid	245.10	1.829	(Ca-H)+3(Ca-NO ₂)+2(Ca-OH)	133.01	1.843	1.843	0.765
2,4-Dinitrotoluene	182.14	1.521	3(Ca-H)+2(Ca-NO ₂)+2(Ca-CH ₃)	120.99	1.505	1.505	1.052
2,4,6-Trinitrotoluene (TNT)	227.13	1.654	2(Ca-H)+3(Ca-NO ₂)+2(Ca-CH ₃)	138.81	1.636	1.636	1.088
2,3,4-Trinitrotoluene	227.13	1.620	2(Ca-H)+3(Ca-NO ₂)+2(Ca-CH ₃)	138.81	1.636	1.636	0.998
2,4,5-Trinitrotoluene	227.13	1.620	2(Ca-H)+3(Ca-NO ₂)+2(Ca-CH ₃)	138.81	1.636	1.636	0.998
2,4,6-Trinitro-m-xylene	241.16	1.604	(Ca-H)+3(Ca-NO ₂)+2(Ca-CH ₃)	152.89	1.577	1.577	1.683
2,3,6-Trinitro-p-xylene	241.16	1.590	(Ca-H)+3(Ca-NO ₂)+2(Ca-CH ₃)	152.89	1.577	1.577	0.818
1,3,5-Trimethyl-2,4,6-trinitrobenzene	255.19	1.48	3(Ca-NO ₂)+3(Ca-NH ₂)	166.98	1.528	1.528	3.243
2,4-Dinitraniline	183.12	1.615	3(Ca-H)+2(Ca-NO ₂)+2(Ca-NH ₂)	110.69	1.654	1.654	2.415
2,4,6-Trinitroaniline	228.12	1.762	2(Ca-H)+3(Ca-NO ₂)+2(Ca-NH ₂)	128.51	1.775	1.775	0.744
2,3,4,6-Tetrinitroaniline	273.12	1.867	(Ca-H)+4(Ca-NO ₂)+2(Ca-NH ₂)	146.33	1.867	1.867	0.600
1,3-Diainino-2,4,6-trinitrobenzene	213.14	1.837	(Ca-H)+3(Ca-NO ₂)+2(Ca-NH ₂)	132.30	1.838	1.838	0.654
1,3,5-Triainino-2,4,6-trinitrobenzene	258.15	1.938	3(Ca-O ₂)+3(Ca-NO ₂)	136.08	1.897	1.897	2.113
3-Methyl-2,4,6-trinitrophenol	243.13	1.69	(Ca-H)+3(Ca-NO ₂)+2(Ca-OH)+2(Ca-CH ₃)	142.41	1.767	1.767	1.006

*Ca designates an aromatic carbon atom.

Average Density = 1.692 g/cm³

Average % Error = 1.286%

Number of Compounds with 0-1% Error = 11

Number of Compounds with 1-2% Error = 9

Number of Compounds with 2-3% Error = 5

Table 2
CALCULATED GROUP MOLAR VOLUMES FOR ALIPHATIC COMPOUNDS

<u>Group Configuration</u>	<u>Letter Designation</u>	<u>Calculated Molar Volume</u>	<u>cm³/mol</u>
C-C, H ₃	a	30.68	
C-C, H ₂ , NO ₂	b	42.61	
C-C ₂ , H ₂	c	15.69	
C-C ₂ , H, NO ₂	d	29.16	
C-C(NO ₂) ₃	e	73.60	
C-C, H, (NO ₂) ₂	f	59.12	
C-C ₂ , (NO ₂) ₂	g	40.87	
C-C, O, =O	h	21.88	
C-C, H ₂ , O	i	16.84	
C-C, H ₂ , OH	j	29.61	
C-C, H ₂ , F	k	30.68	
C-C ₂ , H, OH	l	15.12	
C-C ₃ , OH	m	1.94	
C-C, =O, OH	n	21.98	
C-C, H, =C	o	12.11	
C-C, H ₂ , ONO ₂ (PETN)	p	34.41	
C-H ₂ , =C	q	20.05	
C-C, F ₂ , NO ₂	r	59.92	
C-C ₂ , F ₂	s	25.63	
C-C, F ₃	t	46.28	
C-C, F, (NO ₂) ₂	u	68.81	
C-H ₂ , O ₂	v	27.91	
C-C, H ₂ , ONO ₂ (NG)	w	51.21	
C-C ₄	x	41.49	
C-C ₃ , NO ₂	y	71.23	
C-C ₂ , H, ONO ₂	z	40.39	

Table 3
DENSITY ESTIMATIONS FOR ALIPHATIC COMPOUNDS CONTAINING NO_2 , OH , F , CO_2H AND ONO_2 GROUPS

Compound	Molecular Weight	Measured Density (g/cm ³)	Groups Present*		Calculated Molar Volume	Calculated Density	% Error
			Groups Present*	Molar Volume			
(1) $\text{CH}_3\text{-CH}_2\text{-NO}_2$	75.07	1.045	a+b	73.29	1.024	1.98	
(2) $\text{CH}_3\text{-(CH}_2\text{)}_2\text{-NO}_2$	89.09	1.008	a+b+c	88.98	1.001	0.67	
(3) $\text{CH}_3\text{-(CH}_2\text{)}_3\text{-NO}_2$	103.12	0.971	a+b+c	104.67	0.9852	1.46	
(4) $\text{CH}_3\text{-(CH}_2\text{)}_4\text{-NO}_2$	131.18	0.949	a+b+c	136.05	0.9642	1.60	
(5) $\text{CH}_3\text{-CH-CH}_3$	89.09	0.988	2a+d	90.52	0.9842	0.38	
(6) $\text{O}_2\text{NCH}_2\text{-CH}_2\text{NO}_2$	120.06	1.46	2b	85.22	1.409	3.49	
(7) $(\text{O}_2\text{N})_3\text{C-C}(\text{NO}_2)_3$	300.05	1.998	2e	147.20	2.038	2.00	
(8) $\text{CH}_3\text{-CH-CH}_2\text{-CH}_3$	103.12	0.985	2a+c+d	106.21	0.9709	1.43	
(9) $\text{CH}_3\text{-CH}(\text{NO}_2)_2$	120.06	1.350	a+f	89.80	1.337	0.97	
(10) $\text{CH}_3\text{-CH}_2\text{-CH}(\text{NO}_2)_2$	134.09	1.261	a+c+f	105.49	1.271	0.80	
(11) $\text{O}_2\text{NCH}_2\text{-CH}_2\text{-CH}_2\text{NO}_2$	134.09	1.353	2b+c	100.91	1.329	1.77	
(12) $\text{CH}_3\text{-C}(\text{NO}_2)_2\text{-CH}_3$	134.09	1.30	2a+g	102.23	1.312	0.90	
(13) $\text{O}_2\text{NCH}_2\text{-C(=O)CH}_2\text{-CH}_3$	133.10	1.1953	a+b+h+i	112.01	1.1883	0.59	
(14) $\text{HO-CH}_2\text{-CH}_2\text{-NO}_2$	91.07	1.270	b+j	72.22	1.261	0.71	
(15) $\text{CH}_3\text{-CH}_2\text{-OH}$	46.07	0.7893	a+j	60.29	0.7641	3.19	
(16) $\text{CH}_3\text{-(CH}_2\text{)}_2\text{-OH}$	60.10	0.8035	a+c+j	75.98	0.7910	1.56	
(17) $\text{CH}_3\text{-CH-CH}_3$	60.10	0.7855	2a+1	76.48	0.7858	0.04	
(18) $\text{CH}_3\text{-CH-CH}_2\text{-OH}$	105.09	1.1841	a+d+j	89.45	1.1748	0.78	
(19) $(\text{CH}_3)_3\text{C-OH}$	74.12	0.7887	3a+m	93.98	0.7887	-	

Table 3 (Continued)

DENSITY ESTIMATION FOR ALIPHATIC COMPOUNDS CONTAINING NO_2 , OH, F, CO_2H AND ONO_2 GROUPS

Compound	Molecular Weight	Measured Density (g/cm ³)	Groups Present*		Calculated Molar Volume	Calculated Density	% Error
			a+2c+j	a+3c+j			
(20) $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{OH}$	74.12	0.8098			91.67	0.8086	0.15
(21) $\text{CH}_3-\underset{\text{OH}}{\text{CH}}-\text{CH}_2-\text{CH}_3$	74.12	0.8080	2a+c+1	2a+c+1	92.17	0.8042	0.47
NO ₂							
(22) $\text{C}_2\text{H}_5-\underset{\text{NO}_2}{\text{CH}}-\text{CH}_2-\text{OH}$	119.12	1.1332	a+c+d+j		105.14	1.1330	0.02
(23) $\text{CH}_3-(\text{CH}_2)_4-\text{OH}$	88.15	0.8144	a+3c+j		107.36	0.8211	0.82
OH							
(24) $\text{CH}_3-\underset{\text{OH}}{\text{CH}}-(\text{CH}_2)_2-\text{CH}_3$	88.15	0.8103	2a+2c+1		107.86	0.8173	0.86
OH							
(25) $\text{C}_2\text{H}_5-\underset{\text{OH}}{\text{CH}}-\text{C}_2\text{H}_5$	88.15	0.8212	2a+2c+1		107.86	0.8173	0.48
(26) $\text{HO}_2\text{C}-\text{CO}_2\text{H}$	90.03	1.900	2n		43.96	2.048	7.79
(27) $\text{HO}_2\text{C}-\text{CH}_2-\text{CO}_2\text{H}$	104.06	1.619	c+2n		59.65	1.745	7.75
(28) $\text{HO}_2\text{C}-(\text{CH}_2)_2-\text{CO}_2\text{H}$	118.09	1.572	2c+2n		75.34	1.567	0.29
(29) $\text{HO}_2\text{C}-(\text{CH}_2)_3-\text{CO}_2\text{H}$	132.12	1.424	3c+2n		91.03	1.451	1.92
(30) $\text{HO}_2\text{C}-(\text{CH}_2)_4-\text{CO}_2\text{H}$	146.14	1.360	4c+2n		106.72	1.369	0.69
(31) $\text{HO}_2\text{C}-(\text{CH}_2)_8-\text{CO}_2\text{H}$	202.25	1.2705	8c+2n		169.48	1.1934	6.07
(32) $\text{C}_2\text{H}_5-\underset{\underset{\text{O}}{\parallel}}{\text{C}}-\text{O}-\text{CH}_2-\underset{\underset{\text{O}}{\parallel}}{\text{C}}-\text{O}-\text{C}_2\text{H}_5$	160.17	1.0551	2a+c+2h+2i		154.49	1.0368	1.74
O							
(33) $\text{C}_2\text{H}_5-\text{CO}_2-(\text{CH}_2)_2-\text{CO}_2-\text{C}_2\text{H}_5$	174.20	1.0402	2(a+c+h+l)		170.18	1.0236	1.59
(34) $\text{C}_2\text{H}_5-\text{CO}_2-(\text{CH}_2)_3-\text{CO}_2-\text{C}_2\text{H}_5$	188.22	1.0220	2a+3c+2h+2i		185.87	1.0126	0.92
(35) $\text{C}_2\text{H}_5-\text{CO}_2-(\text{CH}_2)_4-\text{CO}_2-\text{C}_2\text{H}_5$	202.25	1.0076	2(a+2c+h+l)		201.56	1.0034	0.41
(36) $\text{C}(\text{NO}_2)_3-\text{CH}_2-\text{CO}_2-\text{CO}_2-\text{CH}_2-\text{C}(\text{NO}_2)_3$	416.12	-	2(c+h+l)		224.64	1.852	-
(37) $\text{C}(\text{NO}_2)_3-\text{CH}_2\text{CO}_2-\text{CH}_2-\text{CO}_2-\text{CH}_2-\text{C}(\text{NO}_2)_3$	430.15	1.75	c+2(c+h+l)		240.33	1.790	2.29

Table 3 (Continued)
DENSITY ESTIMATIONS FOR ALIPHATIC COMPOUNDS CONTAINING NO_2 , OH , F , CO_2H AND ONO_2 GROUPS

Compound	Molecular Weight	Measured Density (g./cm. ³)	Groups Present*	Calculated Molar Volume	Calculated Density	Error
(38) $\text{C}(\text{NO}_2)_3\text{-CH}_2\text{-CO}_2\text{-CO}_2\text{-(CH}_2\text{)}_2\text{-CO}_2\text{-CH}_2\text{-C}(\text{NO}_2)_3$	444.18	-	2(c+e+h+i)	256.02	1.735	-
(39) $\text{C}(\text{NO}_2)_3\text{-CH}_2\text{-CO}_2\text{-(CH}_2\text{)}_3\text{-CO}_2\text{-CH}_2\text{-C}(\text{NO}_2)_3$	458.21	1.67	3c+2(e+h+i)	271.71	1.686	0.96
(40) $\text{C}(\text{NO}_2)_3\text{-CH}_2\text{-CO}_2\text{-(CH}_2\text{)}_4\text{-CO}_2\text{-CH}_2\text{-C}(\text{NO}_2)_3$	472.23	1.64	4c+2(e+h+i)	287.40	1.643	0.18
(41) $\text{C}(\text{NO}_2)_3\text{-CH}_2\text{-CO}_2\text{-(CH}_2\text{)}_5\text{-CO}_2\text{-CH}_2\text{-C}(\text{NO}_2)_3$	486.26	1.63	5c+2(e+h+i)	303.09	1.604	1.60
(42) $\text{C}(\text{NO}_2)_3\text{-CH}_2\text{-CO}_2\text{-(CH}_2\text{)}_6\text{-CO}_2\text{-CH}_2\text{-C}(\text{NO}_2)_3$	500.29	1.59	6c+2(e+h+i)	318.78	1.569	1.32
(43) $\text{C}(\text{NO}_2)_3\text{-CH}_2\text{-CO}_2\text{-(CH}_2\text{)}_7\text{-CO}_2\text{-CH}_2\text{-C}(\text{NO}_2)_3$	514.31	1.475	7c+2(e+h+i)	334.47	1.538	4.27
(44) $\text{C}(\text{NO}_2)_3\text{-CH}_2\text{-CO}_2\text{-(CH}_2\text{)}_8\text{-CO}_2\text{-CH}_2\text{-C}(\text{NO}_2)_3$	528.34	1.45	8c+2(e+h+i)	350.16	1.509	4.07
(45) $\text{CH}_3\text{-C}(\text{NO}_2)_2\text{-CH}_2\text{-CO}_2\text{-CH=CH-CO}_2\text{-CO}_2\text{-C}(\text{NO}_2)_2\text{-CH}_3$	380.22	1.60	2(a+g+h+i+o)	244.76	1.553	2.91
(46) $\text{HO}_2\text{C-CH=CH-CO}_2\text{H}$	116.07	1.635	2(n+o)	68.18	1.702	4.12
(47) $\text{C}_2\text{H}_7\text{-CO}_2\text{CH=CH-CO}_2\text{-CH=CO}_2\text{-C}_3\text{H}_7$	200.23	1.0129	2(a+c+h+i+o)	194.40	1.0300	1.69
(48) $\text{C}(\text{NO}_2)_3\text{-}(\text{CH}_2\text{)}_2\text{-CO}_2\text{-CH}_2\text{-C}(\text{NO}_2)_2\text{-CH}_3$	355.17	1.68	a+2c+e+g+h+i	215.25	1.650	1.78
(49) $\text{C}(\text{NO}_2)_3\text{-}(\text{CH}_2\text{)}_2\text{-CO}_2\text{-(CH}_2\text{)}_2\text{-CO}_2\text{-(CH}_2\text{)}_2\text{-C}(\text{NO}_2)_3$	472.23	1.63	2(2c+e+h+i)	287.40	1.6431	0.80
(50) $\text{C}_3\text{H}_7\text{-CO}_2\text{-(CH}_2\text{)}_2\text{-CO}_2\text{-C}_3\text{H}_7$	202.25	1.002	2(a+2c+h+i)	201.56	1.0034	0.14
(51) $\text{CH}_3\text{-C}(\text{NO}_2)_2\text{-CH}_2\text{-CO}_2\text{-(CH}_2\text{)}_2\text{-CO}_2\text{-CH}_2\text{-C}(\text{NO}_2)_2\text{-CH}_3$	382.24	1.51	2(a+c+g+h+i)	251.92	1.5173	0.48
(52) $\text{CH}_3\text{-C}(\text{NO}_2)_2\text{-CH}_2\text{-CO}_2\text{-CH=CH}_2$	204.14	1.47	a+g+h+i+o+q	142.43	1.4333	2.50
(53) $\text{C}_2\text{H}_5\text{-CO}_2\text{-(CH}_2\text{)}_2\text{-C}(\text{NO}_2)_2\text{CH}_3$	220.18	1.28	2a+2c+g+h+i	172.33	1.2777	0.18
(54) $\text{C}_2\text{H}_5\text{-CO}_2\text{-C}_3\text{H}_7$	116.16	0.8785	2a+2c+h+i	131.46	0.8836	0.58
(55) $\text{C}(\text{NO}_2)_3\text{-}(\text{CH}_2\text{)}_2\text{-CO}_2\text{-CH}_2\text{-C}(\text{NO}_2)_3$	386.14	1.783	2c+2e+h+i	217.30	1.770	{0.34 0.57}
(56) $\text{CF}_2\text{NO}_2\text{-CF}_2\text{NO}_2$	192.02	1.6024	2r	119.84	1.6023	-
(57) $\text{C}_3\text{H}_7\text{-F}$	62.09	0.7956	a+c+k	77.05	0.8058	1.29
(58) $\text{FCH}_2\text{-CH}_2\text{-CH}_2\text{F}$	80.08	1.0057	c+2k	77.05	1.0393	3.34
(59) $\text{CH}_3\text{-CF}_2\text{-CH}_3$	80.08	0.9205	2a+s	86.99	0.9206	-
(60) $\text{CF}_3\text{-CH}_2\text{-CH}_2\text{-NO}_2$	143.06	1.4205	b+c+t	104.59	1.3678	3.70
(61) $\text{CF}_3\text{-CH}_2\text{-NO}_2$	129.04	1.3914	b+t	88.89	1.4517	4.33

Table 3 (Concluded)

DENSITY ESTIMATIONS FOR ALIPHATIC COMPOUNDS CONTAINING NO_2 , OH , F , CO_2H AND ONO_2 GROUPS

Compound	Molecular Weight	Measured Density (g/cm^3)	Groups Present*	Calculated Molar Volume	Calculated Density	% Error
(62) $\text{CF}(\text{NO}_2)_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{O}-\text{CH}_2-\text{CF}(\text{NO}_2)_2$	320.12	1.607	2(1+u)+v	199.20	1.607	-
(63) PETN $\text{C}(\text{CH}_2\text{ONO}_2)_4$	316.14	1.77	4p+x	179.13	1.7649	0.29
(64) $\text{CH}_3-\text{CH}_2\text{ONO}_2$	91.07	1.100	a+w	81.89	1.1121	1.10
(65) $\text{O}_2\text{NOCH}_2-\text{CH}_2\text{ONO}_2$	152.06	1.48	2w	102.42	1.4847	0.32
(66) $\text{CH}_3-\text{C}(\text{CH}_2\text{ONO}_2)_3$	255.14	1.47	a+3p+x	175.40	1.4546	1.05
(67) $\text{HOCH}_2-\text{C}(\text{CH}_2\text{ONO}_2)_3$	271.14	1.54	j+3p+x	174.33	1.5553	1.00
(68) $\text{O}_2\text{N}-\text{C}(\text{CH}_2\text{ONO}_2)_3$	285.11	1.64	3p+y	174.46	1.64	-
(69) NG $\text{O}_2\text{NOCH}_2-\text{CH}-\text{CH}_2\text{ONO}_2$	227.09	1.596	2w+z	142.81	1.5902	0.37
(70) $\text{O}_2\text{NOCH}_2-\text{C}(\text{CH}_2\text{ONO}_2)_3$	452.15	1.73	2(w+2z)	263.98	1.7128	0.99
(71) $\text{O}_2\text{NOCH}_2-\text{CH}_2-\text{CH}-\text{CH}_2\text{ONO}_2$	241.11	1.52	c+2w+z	158.50	1.5212	0.08
(72) $\text{O}_2\text{NO}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2\text{ONO}_2$	196.12	1.38	2(1+w)	136.10	1.441	5.87
(73) $\text{O}_2\text{NO}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2\text{ONO}_2$	226.14	1.33	2i+v+2w	161.01	1.3788	3.67
(74) $\text{O}_2\text{NO}-\text{CH}_2-\text{CH}-\text{CH}_2-\text{CO}_2-\text{CH}-\text{CH}_3$	299.15	1.47	a+h+1+w+2z	201.39	1.4654	1.05
(75) $(\text{O}_2\text{NO}-\text{CH}_2)_3-\text{C}-\text{CH}_2-\text{O}-\text{CH}_2-\text{C}(\text{CH}_2\text{ONO}_2)_3$	524.26	1.63	2(1+3p+x)	323.12	1.6225	0.46
(76) $(\text{O}_2\text{NOCH}_2)_3-\text{C}-\text{CH}_2-\text{O}-\text{CH}_2-\text{C}(\text{CH}_2\text{ONO}_2)_3$	732.39	1.58	4i+8p+3x	467.11	1.5679	0.76
(77) $\text{FCH}_2-\text{CH}_2-\text{OH}$	64.06	1.104	j+k	60.19	1.063	3.71

Average Density (75 known) = $1.294 \text{ g}/\text{cm}^3$
 Average % Error (71 compounds) = 1.696%
 $1.294 \pm 0.022 \text{ g}/\text{cm}^3$

No. of compounds with 0-1% Error = 34
 No. of compounds with 1-2% Error = 20
 No. of compounds with 2-3% Error = 3
 No. of compounds with 3-4% Error = 6
 No. of compounds with 4-5% Error = 4
 No. of compounds with >5% Error = 4

*See Table 2 for definitions.

Table 4
CALCULATED GROUP MOLAR VOLUMES FOR VARIOUS NITROGEN COMPOUNDS

<u>Group Configuration</u>	<u>Letter Designation</u>	<u>Calculated Molar Volume cm³/mol</u>
C-C, H ₂ , NH ₂	α	34.67
C-C ₂ , H, NH ₂	β	22.49
C-C, H ₂ , NH	γ	20.64
C-C ₂ , H, NH	δ	8.42
C-H ₃ , NH	ε	32.87
C-C, H ₂ , N	η	16.09
C-H ₃ , N	θ	31.00
C-C, H ₂ , N-NO ₂	κ	27.30
C-C ₂ , H, N-NO ₂	λ	9.70
C-H ₃ , N-NO ₂	ξ	37.46
[C-H ₂ , O, N-NO ₂] _C	σ	28.02
C-O ₄	τ	28.45
C-H, O ₃	φ	26.63
C-H ₂ , O ₂ *	ν	28.66
C-C, F, (NO ₂) ₂ #	υ	65.83
C-C, O, F ₂	χ	26.78
C-C ₃ , H	ψ	2.96
(C-C ₂ , H ₂) _C	ca	18.38
[C-H ₂ , (N-NO ₂) ₂] _C †	cb	41.60
(C-C ₂ , H ₂) _{C=8} ‡	--	16.80
[C-H ₂ , (N-NO ₂) ₂] _{C=8}	--	40.02
(C-C, H ₂ , O) _C	cc	21.75
(C-C, H, =C) _C	cd	15.12
(C-H, O, =C) _C	ce	20.66
(C-H, =C, NH) _C	cf	19.81
(N-C, H, NH) _C	cg	11.45

Table 4 (Concluded)

CALCULATED GROUP MOLAR VOLUMES FOR VARIOUS NITROGEN COMPOUNDS

Group Configuration	Letter Designation	Calculated Molar Volume cm ³
(C-H, =C, N) _c +(C-H, N, =N) _c	ch	46.27
(C-C, H ₂ , NH) _c	ci	22.35
(C-C ₂ , =O) _c	cj	13.44
(C-C ₂ , H, NO ₂) _c	ck	31.58
(C-C ₂ , H, OH) _c	cl	12.17
(C-C ₄) _c	cm	24.67
(C-O ₄) _c	cn	11.63
(C-NO ₂ , O, =C) _c	co	33.53
(C-C, F, =C) _c	cp	20.21
(C-C, H, O, NO ₂) _c	cq	36.04
[C-C ₂ , (NO ₂) ₂] _c	cr	43.56
[C-(N-NO ₂) ₂ , =O] _c	cs	36.66
[C-C, H, (N-NO ₂) ₂] _c	ct	42.68
[C-C, F, (N-NO ₂) ₂] _c	cu	47.77
[C-F ₂ , (N-NO ₂) ₂] _c	cv	51.78
(C-C ₂ , =N) _c +(N-O, =C) _c	cw	15.92
(C-H, C, =N) _c +(N-O, =C) _c	cx	28.28
(C-C, N, =N) _c +(N-C, =C) _c	cy	11.82
(C-C, O, =N) _c +(N-O, =C) _c	cz	20.38
C _a -N(H, C) ^{†‡}	-	20.38
C _a -N(C, C)	-	8.54
C _a -N(C, NO ₂)	-	21.66

*This group was listed in Table 2. Consideration of more compounds containing this group has resulted in an improved value of its molar volume.

†Subscript "c" denotes a group from a cyclic compound containing a 5- or 6-membered ring.

‡Subscript "c=8" denotes a group from an 8-membered ring.

**As in Table 1, C_a designates an aromatic carbon atom.

Table 5
DENSITY ESTIMATIONS FOR AMINES, NITRAMINES, AND VARIOUS CYCLIC COMPOUNDS

Compound	Molecular weight	Measured Density, g/cm ³	Groups present*	Calculated molar volume	Calculated density	% Error
1. H ₂ N-CH ₂ -CH ₂ NH ₂	60.11	0.8995	2 α	69.34	0.8669	3.63
2. CH ₃ -CH-CH ₂ -NH ₂	74.13	0.8584	a+α+β	87.84	0.8439	1.69
3. NH ₂ -CH ₂ -CH ₂ -CH ₂ -NH ₂	74.13	0.884	c+2α	85.03	0.8718	1.38
4. H ₂ N-(CH ₂) ₂ → ₄ NH ₂	88.15	0.877	2c+2α	100.72	0.8752	0.21
5. CH ₃ -(CH ₂) ₂ → ₃ NH ₂	73.14	0.7414	a+2c+α	96.73	0.7561	1.99
6. CH ₃ -CH-CH ₂ -CH ₃	73.14	0.724	2a+c+β	99.54	0.7348	1.49
7. CH ₃ ←(CH ₂) ₂ → ₃ NH-C ₂ H ₅	101.19	0.7398	2a+2c+2γ	134.02	0.7550	2.06
8. CH ₃ -CH ₂ -CH-NH-C ₂ H ₅	101.19	0.7396	3a+c+γ+δ	136.79	0.7397	0.02
9. (C ₂ H ₅) ₂ NH	73.14	0.7056	2a+2γ	102.64	0.7126	0.99
10. (CH ₃) ₂ NH	45.09	0.6804	2ε	65.74	0.6859	0.81
11. (C ₅ H ₁₁) ₂ NH	157.30	0.7771	2a+6c+2γ	196.78	0.7994	2.87
12. (C ₄ H ₉) ₂ NH	129.25	0.7670	2a+4c+2γ	165.40	0.7814	1.88
13. (C ₃ H ₇) ₂ NH	101.19	0.7400	2a+2c+2γ	134.02	0.7550	2.03
14. [(CH ₃) ₂ CH] ₂ NH	101.19	0.7169	4a+2δ	139.56	0.7251	1.14
15. H ₂ N-(CH ₂) ₂ -NH-(CH ₂) ₂ -OH	104.15	1.0254	j+α+2γ	105.56	0.9866	3.78
16. (HO-CH ₂ -CH ₂) ₂ -NH	105.14	1.09664	2j+2γ	100.50	1.0462	4.60
17. HO-CH ₂ → ₂ -NH-CH ₂ -CH-C ₂ H ₅	133.19	1.0310	a+c+j+1+2γ	132.38	1.0061	2.41
18. HO-CH ₂ → ₂ N ₂ I-(CH ₂) ₂ -CH-CH ₃	133.19	1.0331	a+c+j+1+2γ	132.38	1.0061	2.61
19. 	181.33	0.9123	10cα+2δ	200.64	0.9038	0.94

Table 5 (Continued)
DENSITY ESTIMATIONS FOR AMINES, NITRAMINES, AND VARIOUS CYCLIC COMPOUNDS

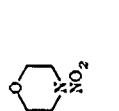
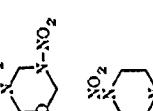
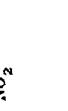
Compound	Molecular weight	Measured density, g/cm ³	Groups present*	Calculated molar volume	Calculated density	% Error
20. $\text{CH}_3\text{-NH-}(\text{CH}_2)_2\text{NH-CH}_3$	88.15	0.828	2v+2e	107.02	0.8237	0.52
21. $(\text{CH}_3)_3\text{N}$	59.11	0.6356	3e	93.00	0.6356	-
22. $(\text{C}_2\text{H}_5)_3\text{N}$	101.13	0.7275	3a+3n	140.31	0.7212	0.87
23. $(\text{C}_3\text{H}_7)_3\text{N}$	143.28	0.7558	3a+3c+3n	187.38	0.7646	1.17
24. $(\text{C}_4\text{H}_9)_3\text{N}$	185.36	0.7771	3a+6c+3n	234.45	0.7906	1.74
25. $[(\text{CH}_3)_2\text{CHCH}_2]_3\text{N}$	185.36	0.7664	6a+3v+3n	241.23	0.7684	-
26. $(\text{C}_5\text{H}_11)_3\text{N}$	227.44	0.7907	3a+9c+3n	281.52	0.8079	2.18
27. $(\text{HOCH}_2\text{CH}_2)_2\text{NC}_2\text{H}_5$	133.19	1.0135	a+2j+3n	138.17	0.9640	4.89
28. $(\text{HOCH}_2\text{CH}_2)_3\text{N}$	149.19	1.1242	3j+3n	137.10	1.0882	3.20
29. $(\text{CH}_3)_2\text{N-NO}_2$	90.08	1.109	2s	74.72	1.2023	8.42
30. $(\text{C}_2\text{H}_5)_2\text{N-NO}_2$	118.14	1.057	2a-2k	115.96	1.0188	3.61
31. $(\text{C}_3\text{H}_7)_2\text{N-NO}_2$	146.19	0.995	2a+2c+2k	147.34	0.9922	0.28
32. $(\text{C}_4\text{H}_9)_2\text{N-NO}_2$	174.24	0.962	2a+4c+2k	178.72	0.9749	1.34
33. $[(\text{CH}_3)_2\text{CH}]_2\text{N-NO}_2$	146.19	1.104	4a+2k	132.42	1.104	-
34. $\text{CH}_3\text{-N}(\text{CH}_2)_2\text{-N-CH}_3$ NO_2	178.15	1.446	$2s+2k$	61.60	1.446	-
35. 	132.12	1.363	2cb+2cc	98.10	1.347	1.19
36. 	178.10	1.824	2c+2cb	97.64	1.824	-
37. 	176.13	1.638	4s	109.20	1.613	1.53

Table 5 (Continued)

DENSITY ESTIMATIONS FOR AMINES, NITRAMINES, AND VARIOUS CYCLIC COMPOUNDS

Compound	Molecular weight	Measured density, g/cm ³	Groups Present*	Calculated molar volume	Calculated density	% Error
38. Cyclopentane	70.14	0.7457	5ca	91.90	0.7632	2.35
39. Cyclohexane	84.16	0.77855	6ca	110.28	0.7631	1.98
40. Cyclooctane	112.22	0.8349	8[C-C ₂ .H ₂] _{c=8}	134.41	0.8349	-
41. RDX	222.12	1.806	3cb	124.80	1.780	1.44
42. HMX	296.16	1.900	4[C-H ₂ .(N-NO ₂) ₂] _{c=8}	160.08	1.850	2.63
43. N-Propylaniline	135.21	0.9443	a+c+1+5[Ca-H] +[Ca-N(H,C)]	142.24	0.9506	0.66
44. N-Methylaniline	107.16	0.98912	θ+5[Ca-H]+[Ca-N(H,C)]	110.78	0.9673	2.20
45. N-Ethylaniline	121.18	0.9625	a+1+5[Ca-H]+[Ca-N(H,C)]	126.55	0.9576	0.51
46. N,N-Diethylaniline	149.24	0.93507	2a+2n+5[Ca-H]+[Ca-N(C,C)]	161.48	0.9242	1.16
47. N,N-Diisopropylaniline	177.29	0.9104	2a+2c+2n+5[Ca-H]+[Ca-N(C,O)]	192.86	0.9193	0.97
48. N-Butylaniline	149.24	0.93226	a+2c+n+5[Ca-H]+[Ca-N(H,C)]	157.93	0.9450	1.37
49. Tetrayl	287.14	1.73	3[Ca-NO ₂] ₂ +2[Ca-H] ₂ +[Ca-N(C,NO ₂)]	165.12	1.739	0.52
50.	72.12	0.8892	2ca+2cc	80.26	0.8986	1.05
51.	86.14	0.8810	3ca+2cc	98.64	0.8733	0.88
52.	68.08	0.9514	2cd+2cc	35.78	0.9514	-
53.	71.12	0.8520	2ca+2ci	81.46	0.8731	2.47



Table 5 (Continued)
DENSITY ESTIMATIONS FOR AMINES, NITRAMINES, AND VARIOUS CYCLIC COMPOUNDS

Compound	Molecular weight	Measured density, g./cm. ³	Groups present*	Calculated molar volume	Calculated density	% Error
54.		85.15	0.8606	3ca+2ci	99.84	0.8529 0.90
55.		67.09	0.9691	2cd+2cf	69.86	0.9603 0.90
56.		69.11	0.9097	ca+cl+cf+cd	75.66	0.9134 0.41
57.		87.12	1.0005	2cc+2ci	88.20	0.9878 1.27
58.		70.10	1.0200	ci+cd+cf+cq	68.73	1.0200 -
59.		68.08	1.0303	cf+ch	66.08	1.0303 -
60.		68.13	0.7720	3ca+2cd	85.38	0.7980 3.36

Table 5 (Continued)
DENSITY ESTIMATIONS FOR AMINES, NITRAMINES, AND VARIOUS CYCLIC COMPOUNDS

Compound	Molecular weight	Measured density, g/cm ³	Groups present*	Calculated molar volume		Calculated density	Error %
				ca	4cd		
61.		66.10	0.8021	ca+4cd		78.86	0.8382
62.		84.19	0.94869	4ca+cj		86.96	0.9681
63.		115.13	1.0776	4ca+ck		105.10	1.0954
64.		82.15	0.8102	4ca+2cd		103.76	0.7917
65.		80.14	0.8405	2ca+4cd		97.24	0.8242
66.		80.14	0.8471	2ca+4cd		97.24	0.8242
67.		98.14	0.9478	5ca+cj		105.34	0.9316
68.		129.16	1.0610	5ca+ck		123.48	1.0460
69.		100.16	0.9624	5ca+c1		104.07	0.9624

Table 5 (Concluded)

DENSITY ESTIMATIONS FOR AMINES, NITRAMINES, AND VARIOUS CYCLIC COMPOUNDS

Compound	Molecular weight	Measured density, g/cm ³	Groups present	Calculated molar volume	Calculated density	% Error
70.	384.22	1.62	2ca+cj+2cm+4p	237.17	1.62	-
71. $(\text{CH}_2\text{ONO}_2)_2$						
72. $\text{C}(\text{OCH}_2\text{CH}_3)_4$	192.26	0.9186	$\tau+4a+4i$	218.53	0.8798	4.22
73. $\text{C}(\text{OC}_2\text{H}_5)_4$	248.36	0.897	$\tau+4a+4c+4i$	281.29	0.8829	1.57
74. $\text{C}[\text{OCH}_2\text{C}(\text{NO}_2)_3]_4$	732.22	1.84	$\tau+4e+4i$	390.21	1.876	1.96
75. $\text{HC}[\text{OC}_2\text{H}_5]_3$	624.19	1.71	$\tau+4i+4u$	359.13	1.738	1.64
76. $\text{HC}[\text{OC}_3\text{H}_7]_3$	148.20	0.8909	$\phi+3a+3i$	169.19	0.8760	1.67
77. $\text{HC}[\text{OCH}_2\text{C}(\text{NO}_2)_3]_3$	190.28	0.8805	$\phi+3a+3c+3i$	216.26	0.8799	0.07
78. $\text{HC}[\text{OCH}_2\text{CF}(\text{NO}_2)_2]_3$	553.18	1.80	$\phi+3e+3i$	297.95	1.8566	3.14
79. $\text{H}_2\text{C}[\text{OC}_2\text{H}_5]_2$	472.15	1.76	$\phi+3i+3u$	274.64	1.719	2.32
80. $\text{H}_2\text{C}(\text{OC}_3\text{H}_7)_2$	104.15	0.8319	$\nu+2a+2i$	123.70	0.8419	1.21
81. $\text{H}_2\text{C}[\text{OCH}_2\text{C}(\text{NO}_2)_3]_2$	122.12	0.8345	$\nu+2a+2c+2i$	155.08	0.7875	5.63
82. $[(\text{NO}_2)_3\text{CCH}_2]_2\text{NNO}_2$	374.13	1.72	$\nu+2e+2i$	209.54	1.7854	3.78
83. $[(\text{NO}_2)_2\text{CCH}_2]_2\text{NNO}_2$	388.15	1.96	$2e+2K$	201.80	1.9234	1.87
	334.13	1.91	$2u+2K$	186.26	1.7939	6.08

Average Density (83 compounds) = 1.0403 g/cm³

Average % Error (70 compounds) = 2.054%

Number of compounds with 0-1% Error = 17

Number of compounds with 1-2% Error = 27

Number of compounds with 2-3% Error = 14

Number of compounds with 3-4% Error = 7

Number of compounds with 4-5% Error = 4

Number of compounds with >5% Error = 23

1.0403 g/cm³ ± 0.0214 g/cm³

*See Table 2 and 1 for definitions.

Table 6

SUMMARY OF THE ACCURACY OF THE
GROUP ADDITIVITY APPROACH TO DENSITY ESTIMATION

<u>% Error Range</u>	<u>Number of Compounds within This Range of Density Estimation Error</u>	<u>% of Compounds Studied with This Range</u>
0-1	62	36.9
1-2	56	33.3
2-3	20	11.9
3-4	15	8.9
4-5	8	4.8
>5	<u>7</u>	<u>4.2</u>
Total	169	100.0

Average Density (179 compounds) = 1.241 g/cm³

Average % Error (168 compounds) = 1.784 %

Average Absolute Error in Density = 0.022 g/cm³

Table 7
DENSITY ESTIMATIONS FOR PROPOSED EXPLOSIVES

Compound	Molecular weight	Groups present*	Calculated molar volume	Calculated density, g/cm ³
1. 	158.07	2cd+2co	97.30	1.6246
2. 	194.05	2co+2cp	107.48	1.8055
3. 	340.16	cn+4cc+2cr	185.75	1.8313 (Measured Density = 1.85) (1.01% Error)
DTGU				
4. 	358.09	2cs+ct	168.85	2.1208
TTGU				
5. 	402.08	2cs+2cu	178.65	2.2506
6. 	366.10	2cu+2cv	168.47	2.1137
7. 	318.10	c+h+i+2u	186.07	1.7096

Table 7 (Concluded)

DENSITY ESTIMATIONS FOR PROPOSED EXPLOSIVES

Compound	Molecular weight	Groups present*	Calculated molar volume	Calculated Density, g/cm ³
8. $\text{F}(\text{NO}_2)_2\text{C}-\text{CH}_2-\text{CF}_2-\text{O}-\text{CH}_2-\text{C}(\text{NO}_2)_2\text{F}$	340.10	c+i+2u+x	190.97	1.7809
9. $\text{F}(\text{NO}_2)_2\text{C}-\text{C}=\text{N}$ 	314.07	2u+cy+cz	163.86	1.9167
10. $\text{F}(\text{NO}_2)_2\text{C}-\text{C}=\text{N}$ 	238.09	u+ck+cc+cw	136.17	1.7485
11. $\text{F}(\text{NO}_2)_2\text{C}-\text{C}=\text{N}$ 	238.09	u+ca+cq+cw	135.08	1.7626
12.	230.14	2a+2cq+2cw	140.68	1.6359 (measured Density = 1.686) (3.12% Error)

* See Tables 2 and 4 for definitions.

II SYNTHESIS OF EXPLOSIVES FOR DENSITY ESTIMATION

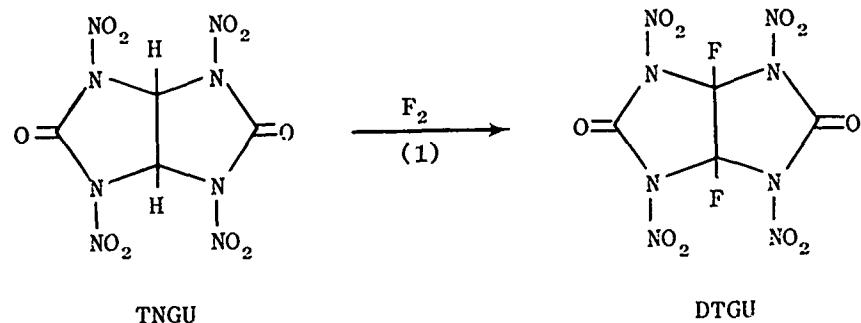
Concurrent with our research on the estimation of density by group additivity techniques, we conducted a synthesis program with the objective of preparing specific nonhydrogen or low-hydrogen explosives and determining their densities. These explosives were new, and for the most part, their syntheses were of an exploratory nature. The choice of compounds to be synthesized was made by agreement among the Project Monitor, Dr. M. J. Kamlet and Dr. H. G. Adolph of NSWC, and Mr. C. L. Coon and Dr. D. L. Ross of SRI. Although none of the target compounds had been prepared previously, most of the synthetic steps were based on known analogous reactions. However, this research should be considered as an exploratory synthetic effort in which the goal was to prepare new and potentially important military explosives.

Fluorination of Tetranitroglycoluril (TNGU)

Tetranitroglycoluril (TNGU), discovered by the French, is a powerful oxidizer that is currently receiving some interest in the United States because of its high density (2.03 g/cm³) and high oxygen balance. One detracting feature, however, is its sensitivity to moisture. Because a fluorinated TNGU molecule was expected to have a higher density and/or lower moisture sensitivity, its synthesis was investigated.

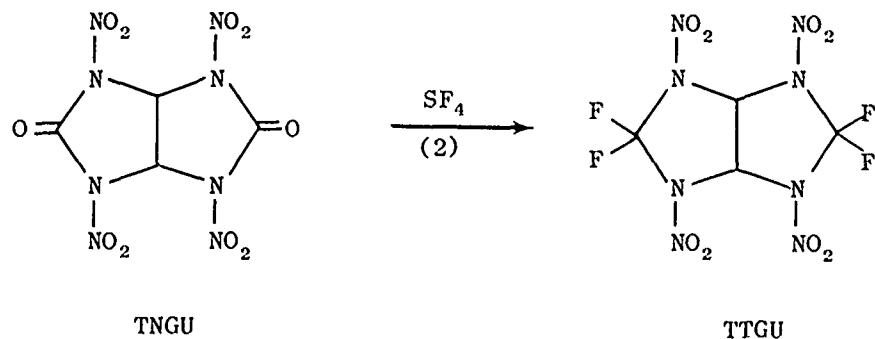
We proposed that fluorine could be incorporated into the basic TNGU structure by two methods. First, TNGU might be fluorinated directly with

elemental fluorine to replace bridgehead hydrogens and give difluorotetra-nitroguycouril (DTGU):



This reaction should give a product with increased density as well as provide a nonhydrogen explosive, a class of explosives of current interest. Precedent for this type of reaction at a tertiary carbon is found in the work of Hesse and Barton.¹ The density of DTGU, estimated previously in this report, is 2.12 g/cm³.

Second, the carbonyl of TNGU might be replaced with difluoromethyl groups by reaction with SF₄ to give 2,2,5,5-tetrafluoro-1,3,4,6-tetranitroimidazolido[4,5-d]imidazoline (TTGU):



The success of this proposed reaction would provide a more dense explosive (estimated density is 2.11 g/cm³) with lower moisture sensitivity than TNGU.

The closest analogy to this reaction is given in the work of de Pasquale,² in which a disubstituted amide is converted to its difluoromethyl derivative.

The reaction of TNGU with elemental fluorine in HF was studied in an effort to fluorinate the bridgehead carbons. A typical reaction was run by dissolving 1.0 g of TNGU in 25 ml of anhydrous hydrofluoric acid in a Kel-F reactor and cooling to -78°C. A mixture of fluorine in nitrogen (1:4) was bubbled through the solution for one hour. A sample of the reaction mixture was removed, and the fluorination was continued for another hour at 0°C. Removal of the hydrofluoric acid by entrainment in N₂ left a mixture of white solid and yellow liquid in both the sample withdrawn and the final product. Although a ¹⁹F nmr analysis of these crude products showed a peak at 150.6 ppm upfield from fluorotrichloromethane, the ¹H analyses indicated that the major portion of the product mixture was TNGU. After multiple recrystallizations from acetone, a very small amount of another product was obtained. The elemental analysis of that product was very close to that expected for dinitroglycoluril. Since dinitroglycoluril might be expected to arise from extensive handling of the product mixture under ambient conditions, the fluorination was repeated on a larger scale, taking care to limit exposure of the reaction mixture to moisture. The ¹H nmr analysis of the crude product again showed that the major component of the product mixture was TNGU.

One additional attempt was made to fluorinate the bridgehead carbons of TNGU, using perchlorylfluoride.³ Ethanol was used as a solvent. Column chromatography of the product resulted in fractions containing mixtures of unknown products, which all contained ethyl groups according to ¹H nmr analysis. Although TNGU exhibits some hydrolytic instability, it was hoped that reaction with the ethanol would not occur.

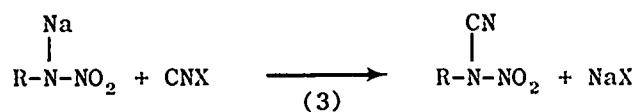
The fluorination of the carbonyl groups of TNGU, Equation (2), was studied using mixtures of SF₄ and HF. The combination of 1 g TNGU,

21 g SF₄, and 19 g HF was sealed in a high-pressure reactor and heated to 100°C for 4 hours. A dark, gummy product was obtained. The ir spectrum of the product did not resemble that of TNGU and did not appear to have any C-F absorption. Apparently, TNGU decomposed under the reaction conditions.

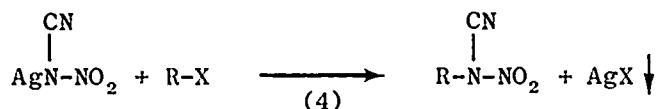
In summary, the fluorination of TNGU with elemental fluorine or with SF₄ appears to be difficult. Future work in this area should be directed toward replacement of the bridgehead hydrogens to TNGU with elemental fluorine or another fluorinating agent. Although we obtained no definable fluorinated product from these reactions, TNGU was stable under most of the reaction conditions used, and a small degree of fluorination was detected by nmr analysis. Furthermore, the nmr fluorine shifts were in the region expected for a fluorine atom on a bridgehead. We would suggest the use of much longer reaction times and perhaps the use of a fluidized-bed fluorination technique to study this reaction further.

Derivatives of Nitrocyanamide

The nitrocyanamide group [-N(NO₂)CN] is of interest when considering the synthesis of new energetic compounds because of its favorable heat of formation, the fact that it contains no hydrogen, and its expected contribution to increased density. Although this group has been known since 1949,⁴ very little work has been done on the synthesis of its derivatives. The only two procedures reported for synthesizing the nitrocyanamide group are by the reaction of cyanogen halide with the salt of nitramine,⁵ Equation (3), and by the reaction of a salt of nitrocyanamide with a reactive halide,⁶ Equation (4).

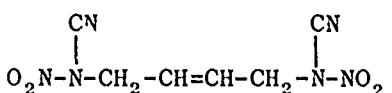
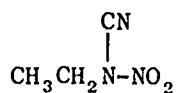
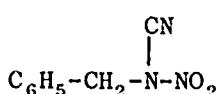
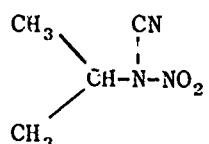
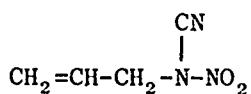
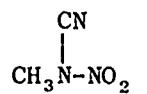


$\text{X} = \text{Br}, \text{I}$

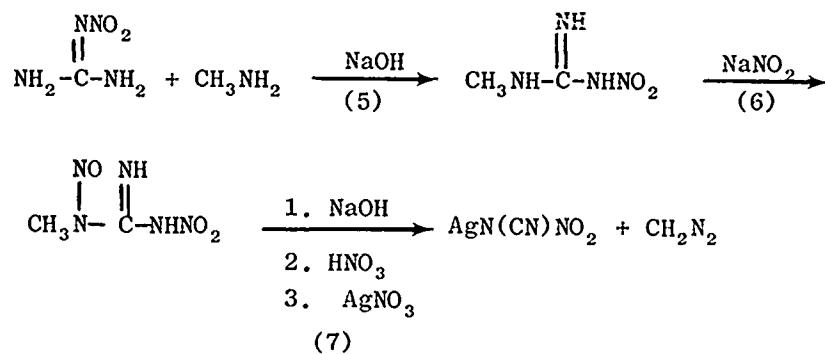


$\text{X} = \text{Br}, \text{I}, \text{Cl}$

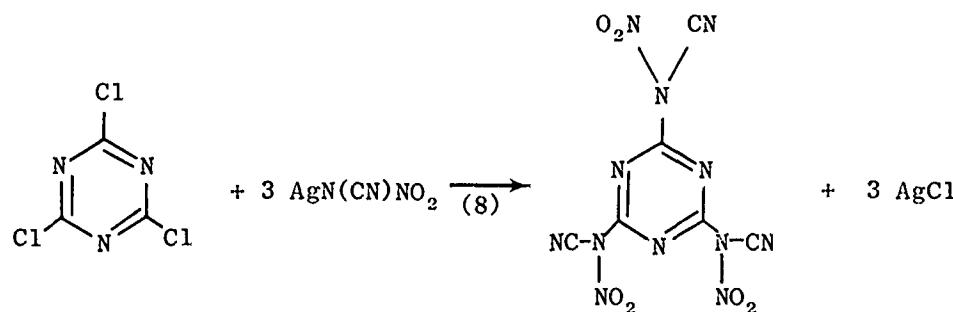
The latter reaction, which was studied briefly in our laboratory, appears to be quite general with aliphatic halides, and derivatives such as the following have been synthesized:



Silver nitrocyanamide is easily prepared from nitroguanidine by an improvement of procedures developed by McKay⁴ and Harris⁷:



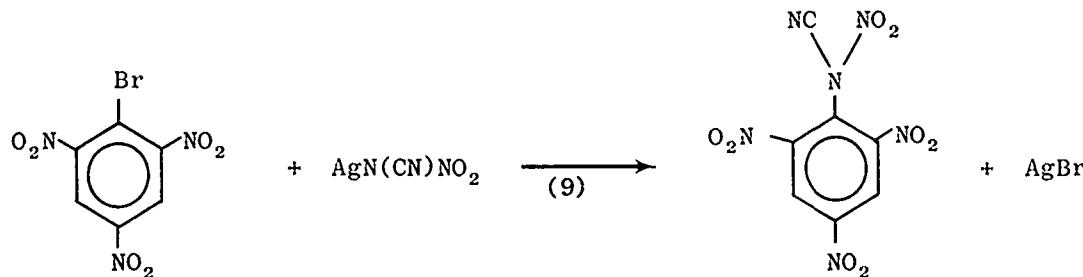
On this project we studied the chemistry of silver nitrocyanamide with the objective of placing three nitrocyanamide groups on a triazine ring:



As part of this study a solution of excess silver nitrocyanamide and cyanuric chloride in acetonitrile was stirred at ambient temperature for 48 hours, during which time a small amount of silver chloride precipitated. The silver chloride, which was collected and dried, represented about 4% of that expected for complete conversion. A

second reaction of silver nitrocyanamide with cyanuric chloride in acetonitrile was run at reflux temperature (82°C). After 24 and 48 hours, 3% and 5%, respectively, of the theoretical quantities of silver chloride had precipitated. Similar reactions were tried using anhydrous acetone as solvent, and very little silver chloride precipitated. A workup of these reactions yielded only starting materials, and no metathetical product was detected.

We also briefly examined the reaction of picryl bromide with silver nitrocyanamide to obtain the picryl derivative shown in Equation (9).

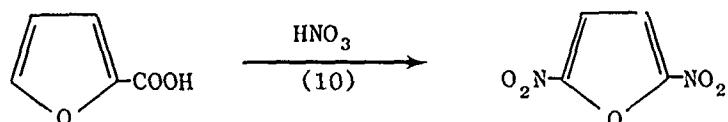


The results of this work were similar to those with cyanuric chloride in that very little reaction occurred; only small quantities of silver bromide were formed even after long reaction times or at elevated temperatures, and no metathetical products were detected. In the case of picryl bromide, the lack of product might be explained by the size of the nitrocyanamide group and the steric problems encountered because of the presence of the adjacent nitro group; this explanation does not hold in the case of cyanuric chloride. However, metathetical reactions with picryl halide and cyanuric chloride have generally not been successful; for example, numerous attempts to react a metal nitrite with these compounds to form a C- NO_2 bond have not been successful.

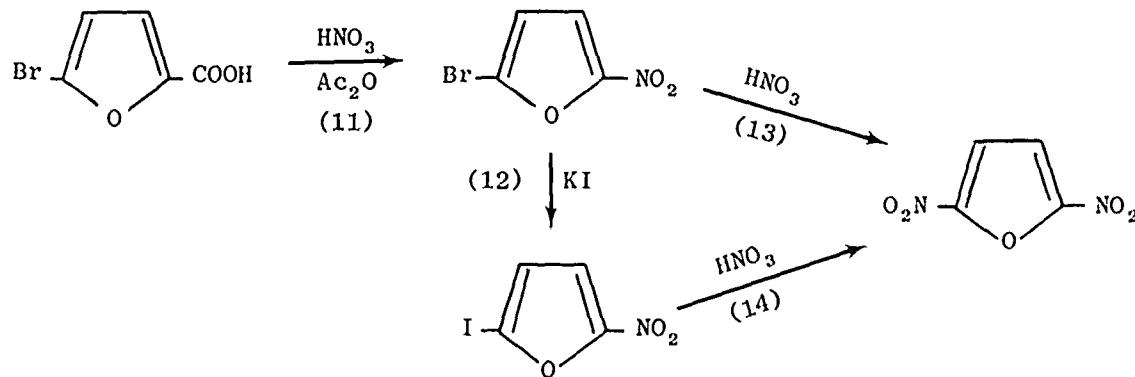
In summary, we feel that further work on the reactions of silver nitrocyanamide with cyanuric chloride or picryl chloride will not be profitable. However, efforts to incorporate the nitrocyanamide group into energetic organic molecules should continue. This group has been largely overlooked by researchers, but its relatively easy synthesis,^{5,6} favorable heat of formation, and possible contribution to density should be considered in future synthetic efforts.

Fluorination of Dinitrofuran (DNF)

2,5-Dinitrofuran was prepared by the method of Hill and White⁸ as shown in Equation (10).

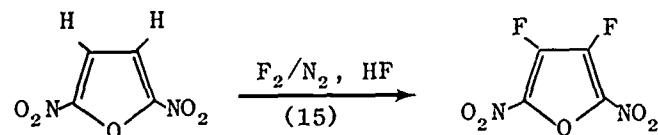


Before using this procedure for the synthesis of 2,5-dinitrofuran, considerable effort was expended in trying to prepare it by the route of Nazarova and Novikov⁹ as shown in Equations (11)-(14).



The synthesis of the intermediates, 5-bromo- and 5-iodo-2-nitrofuran, gave no problems, but numerous attempts to prepare DNF failed. At best, traces of the DNF were detected by thin layer chromatography, but the desired product was never isolated. Also, the bromo and iodo intermediates must be handled with great care to avoid contact with skin. Even dilute concentrations of 5-bromo-2-nitrofuran cause serious burns. It is obvious that the preferred route to DNF is through the procedure of Hill and White; the Russian procedure should be avoided.

Three attempts were made to fluorinate DNF to give the target compound 3,4-difluoro-2,5-dinitrofuran, as shown in Equation (15).



These fluorinations were carried out by bubbling a 30% (v/v) mixture of fluorine in nitrogen through a solution of DNF in anhydrous HF. When the fluorination was run at ambient temperature ($\sim 19^\circ\text{C}$) or at 0°C , the fluorine nmr spectrum of the crude semisolid product exhibited many peaks between 60 and 100 ppm upfield from the fluorotrichloromethane reference. Since the large number of peaks indicated decomposition of DNF, a second fluorination was run at 0°C and at a much lower fluorine concentration (10% v/v) and flow rate. The fluorine nmr spectrum of this product had only four major peaks (69, 83, 91, and 96 ppm) upfield from fluorotrichloromethane. Because these shifts were in the region expected for an aromatic fluorine compound, a separation of products was attempted. Column chromatography of the product on silica gel using 50% methylene chloride in hexane eluted only the starting material. The column was stripped with ethyl acetate and the solvent evaporated, leaving a residue that

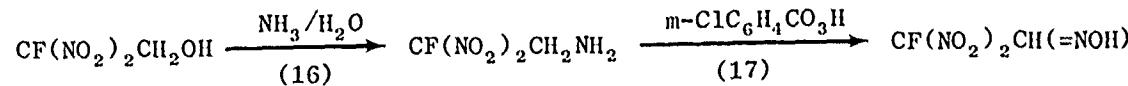
exhibited strong carbonyl and hydroxyl absorptions in the ir spectrum, which indicated that significant decomposition had occurred. Nmr analyses of these products showed no shifts in the aromatic fluorine region that were present in the crude reaction product.

The presence of only four major peaks in the fluorine nmr spectrum indicates that the fluorination was more selective at a lower reaction temperature and fluorine flow rate. Still more selectivity might be possible at temperatures less than 0°C and with slower addition of fluorine. Although it is not confirmed that the desired fluorination is occurring, the presence of relatively few fluorine peaks in the correct region of the nmr spectrum is promising. We feel that continued research on this subject could be productive and suggest fluid-bed fluorination techniques be studied in addition to the low-temperature, low-fluorine system described above.

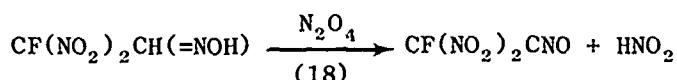
Dipolarophile Additions to Fluorodinitroacetonitrile Oxide (FDNO)

A continued effort was carried out on the reaction of dipolarophiles with fluorodinitroacetonitrile oxide (FDNO). The objective of this phase of our research was to react FDNO with an energetic dipolarophile to form a dense, overoxidized product. This research was based on the work of Adolph¹⁰; the general subject of dipolarophile additions has been extensively reviewed by Huisgen.^{11, 12}

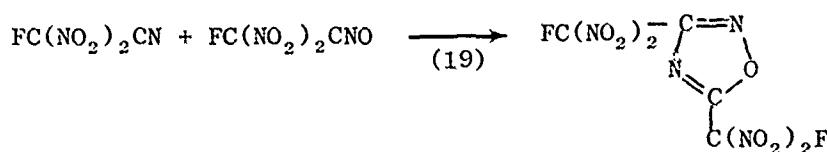
A stock solution of fluorodinitroacetaldoxime, the precursor to FDNO, was prepared by the oxidation of fluorodinitroethylamine with *m*-chloroperbenzoic acid:



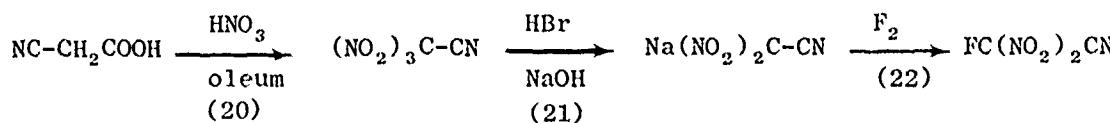
This stock solution of the oxime in methylene chloride was stored at -30°C to prevent isomerization to fluorodinitroacetamide. FDNO was generated as needed by treating the oxime with dinitrogen tetroxide, as in Equation (18).



The reaction of FDNO with fluorodinitroacetonitrile was run with the objective of obtaining the oxadiazole shown in Equation (19).

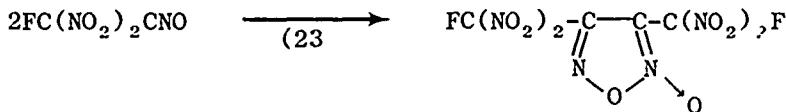


Fluorodinitroacetonitrile was prepared by known procedures,^{13,6} shown in Equations (20)-(22); it can be stored for extended periods of time without decomposition.



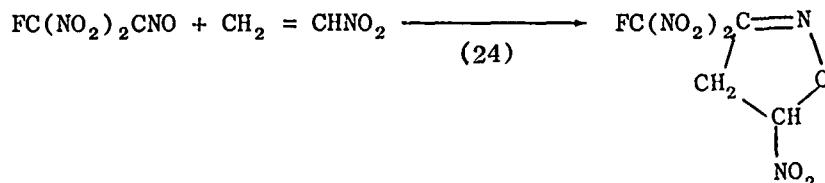
One equivalent of fluorodinitroacetonitrile was added to a solution of the fluorodinitroacetaldoxime/NO₂ adduct,¹⁴ and the resulting solution was heated to form FDNO in situ, which was expected to react with fluorodinitroacetonitrile to form the oxadiazole. The product was a pale yellow liquid and was identified as bis(fluorodinitromethyl)furoxane

by comparison with an authentic sample prepared by the procedure reported by Adolph,¹⁰ Equation (23).

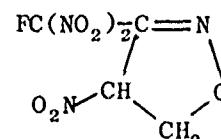


The reaction was repeated using a tenfold excess of fluorodinitroacetonitrile to reduce the probability of self-condensation of FDNO, which results in formation of the furoxane. However, the only product obtained from this reaction was the furoxane. Since the electronegative groups in fluorodinitroacetonitrile should make it very reactive toward FDNO, the fact that the furoxane was the only product indicates that the self-condensation reaction of FDNO is very rapid and the condensation with fluorodinitroacetonitrile was unlikely.

We continued our work on FDNO condensations by studying its reaction with nitroethylene. The expected product from this reaction is a fluorodinitronitroisoxazoline as shown in Equation (24).



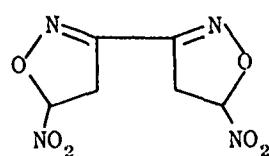
or



The procedure was the same as that used for the attempted additions of fluorodinitroacetonitrile to FDNO. The nitroethylene addition yielded

a yellow liquid that did not contain any bis(fluorodinitromethyl)furoxane, based on ir analysis. The ir spectrum had an absorption corresponding to $-C=N-$, and the proton nmr spectrum indicated the presence of several products that contained the $-CH_2-CH(NO_2)-$ group.

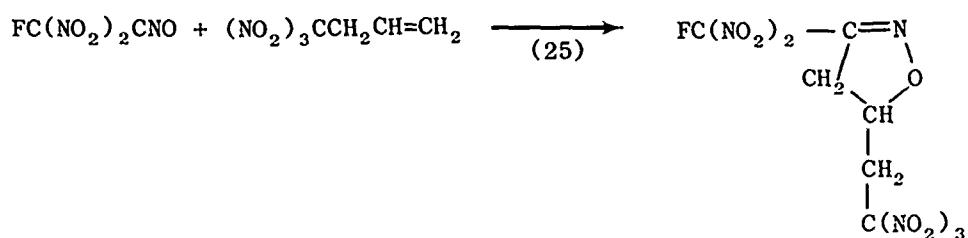
Many attempts were made to separate the products of this reaction by column chromatography and distillation. In general, these attempts were unsuccessful and resulted in little or no separation of the components. However, one chromatographic separation was partially successful. In this separation the crude product was passed through a silica gel column and eluted with varying mixtures of methylene chloride and hexane. At first, the eluant was 20% methylene chloride in hexane, and the percentage of methylene chloride was increased incrementally until 100% methylene chloride was eluting and no more of the product mixture came off the column. The column was then stripped with acetonitrile. All the fractions collected up to fraction 40 appeared to be varying mixtures of reaction products, based on ir and nmr spectra. The nmr spectra of these mixtures very clearly showed the presence of several compounds that contained the $-CH_2-CH(NO_2)-$ moiety, and the ir spectra indicated that ketones and alcohols were present. The rechromatographing of these fractions not only failed to provide further separation of components but also led to small changes in some of the components as shown by their more complex nmr spectra. However, fractions 41 to 47 gave a pure solid product that melted at $145^{\circ}C$ after recrystallization from ethyl acetate/chloroform. Based on the ir and elemental analyses, the mass spectrum, and 1H and ^{13}C nmr spectra, we identified this product as 5,5'-dinitro-3,3'-bi-2-isoxazoline:



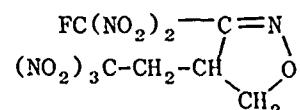
The mass spectrum and the ^1H and ^{13}C nmr spectra are included in the experimental portion of this section.

The density of 5,5'-dinitro-3,3'-bi-2-isoxazoline was found to be 1.686 g/cm³. The estimated density using group additivity techniques was 1.635, which was 3.02% low. Although there is no doubt concerning the structure assigned to this molecule, no acceptable mechanism for its formation has been postulated. Any mechanism must account for the loss of fluorodinitromethyl groups and the formation of a symmetrical dimer. No similar products have been reported in previous research on dipolarophile additions. The mechanism of this reaction would probably be clearer if the other reaction products could be isolated and identified. Because our previous experience with the reaction of FDNO with fluorodinitroacetonitrile indicates that FDNO dimerizes to bis(fluorodinitromethyl)furoxane, as was shown in Equation (23), we suspected that 5,5'-dinitro-3,3'-bi-2-isoxazoline may be a product of the reaction of nitroethylene with the furoxane. Therefore, we prepared a sample of the furoxane and refluxed a solution of the furoxane and nitroethylene in methylene chloride for 16 hours. There was no reaction. This indicates that the isoxazoline is a product of the reaction between FDNO and nitroethylene; therefore, it may be possible to react FDNO with other olefins to yield the desired isoxazoline product.

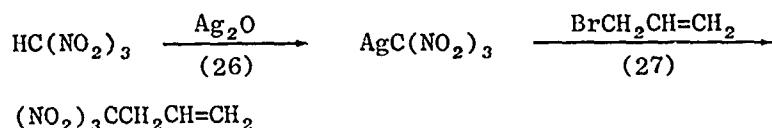
Additional research on dipolarophile additions with FDNO were carried out by studying the reaction of FDNO with 4,4,4-trinitrobutene, as shown in Equation (25).



or



The 4,4,4-trinitrobutene was prepared by the reaction of allyl bromide with silver nitroform as shown in Equations (26) and (27).



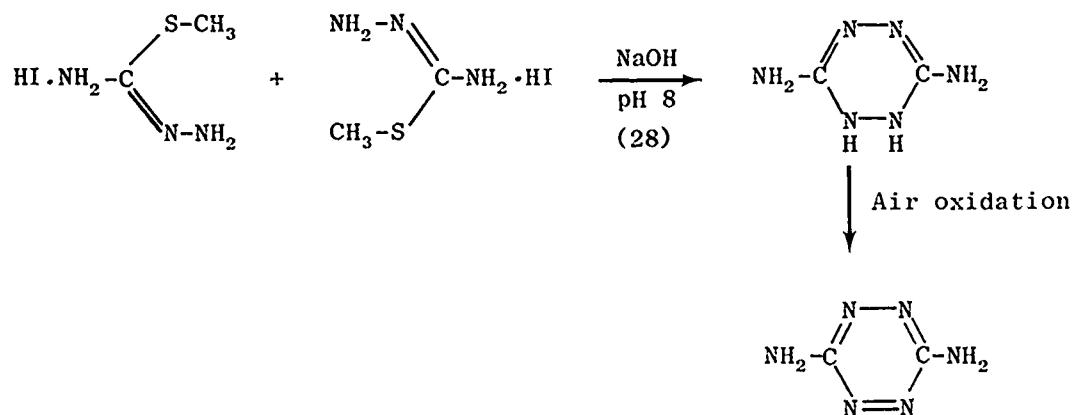
The attempted condensation reaction was run as described above with nitroethylene, and a light-yellow semisolid material was obtained. The ir and nmr spectra of the crude product indicated that it was a mixture of several compounds; however, the nmr spectrum contained peaks corresponding to those expected for the desired product. The presence of the $-\text{CH}_2-\text{CH}[\text{CH}_2\text{C}(\text{NO}_2)_3]-$ moiety was easily discerned by nmr, and ir analysis indicated that the $-\text{CNO}$ group had reacted but that the fluorodinitromethyl group was still present. Extensive thin layer

chromatography and column chromatography using several solid and liquid phases gave mixtures of products. Nmr analyses of the products obtained from liquid chromatography samples show that some separation occurred, but mixtures were always present. These analyses also show that the components of these mixtures are similar and that the trinitroethyl-ethylene group is present in several molecular orientations. Chromatography of fractions from initial chromatographic separation resulted in a further separation of products, but a decomposition of products also was evident by the more complex nmr spectra. No pure products were isolated. Difficulties encountered in our attempts to isolate a product from this reaction are similar to those involved in the isolation of a product from the reaction of nitroethylene with FDNO, in which only 5,5'-dinitro-3,3'-bi-2-isoxazoline was obtained from a complex mixture. 5,5'-Dinitro-3,3'-bi-2-isoxazoline was not isolated from the FDNO-trinitrobutene reaction.

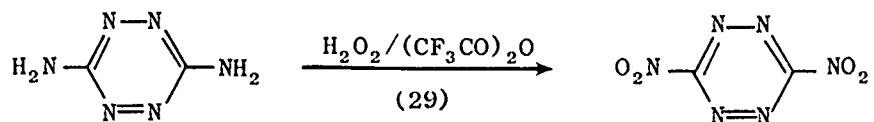
In summary, the addition of energetic dipolarophiles to FDNO appears to be a complex reaction leading to mixtures of compounds whose separation is difficult. Additional research in this area could be useful if more complete separation of reaction products can be effected. Thin layer and high pressure liquid chromatography are attractive techniques that should be considered.

Oxidation of 3,6-Diaminotetrazine

Research was also conducted on the synthesis of 3,6-dinitrotetrazine by the oxidation of 3,6-diaminotetrazine. 3,6-Diaminotetrazine was prepared by the reaction of S-methylthiosemicarbazide hydroiodide with sodium hydroxide,¹⁵ as in Equation (28).

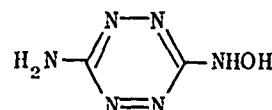


A study of the oxidation of 3,6-diaminotetrazine to 3,6-dinitrotetrazine was carried out using hydrogen peroxide in trifluoroacetic anhydride, as shown in Equation (29). Several oxidations were run and the progress of the reactions followed by hplc.



Vigorous oxidation conditions ($40^{\circ}C$) over a 24-hour period gave complete oxidation of the diamine to gaseous products. Mild oxidation

conditions (< 10°C for 20 minutes) produced one major product based on hplc analysis. Although the structure is unconfirmed, elemental analysis and hplc retention time strongly suggest that the product is 3-amino-6-hydroxylaminotetrazine:



Additional oxidation reactions at ambient temperature for longer times gave mixtures of products. The progress of the reaction was monitored by hplc analysis of small samples, which showed the appearance and disappearance of at least five products. However, none of these products was predominant except the first product formed, which is presumably the hydroxylamine discussed above. Elemental analysis of the product mixture after a reaction period of 3 hours gave an average molecular formula of C₂H₃N₅O₆, which is overoxidized when balanced to CO and water. In addition, these product mixtures are shock sensitive. Very little work was carried out on isolation of the reaction products, although we feel that efforts in this area using column chromatography and hplc would be profitable.

3,5-Bis(nitrimino)-Δ'-1,2,4-triazoline (NTZ)

A brief study of the azo-bis(nitrimino) group was carried out in conjunction with our efforts to synthesize NTZ as shown in Figure 1. The only reference to the synthesis of a compound containing the azo-bis(nitrimino) group was by G. F. Wright in his synth *c's* of azo-bis-nitroformamidine, Equations (30)-(33).¹⁶ He used 100% nitric acid in acetic anhydride to convert the chloroimino group to a nitrimino group. We have prepared this compound on a separate project for Lawrence Livermore Laboratory (LLL) and have supplied LLL with a small sample

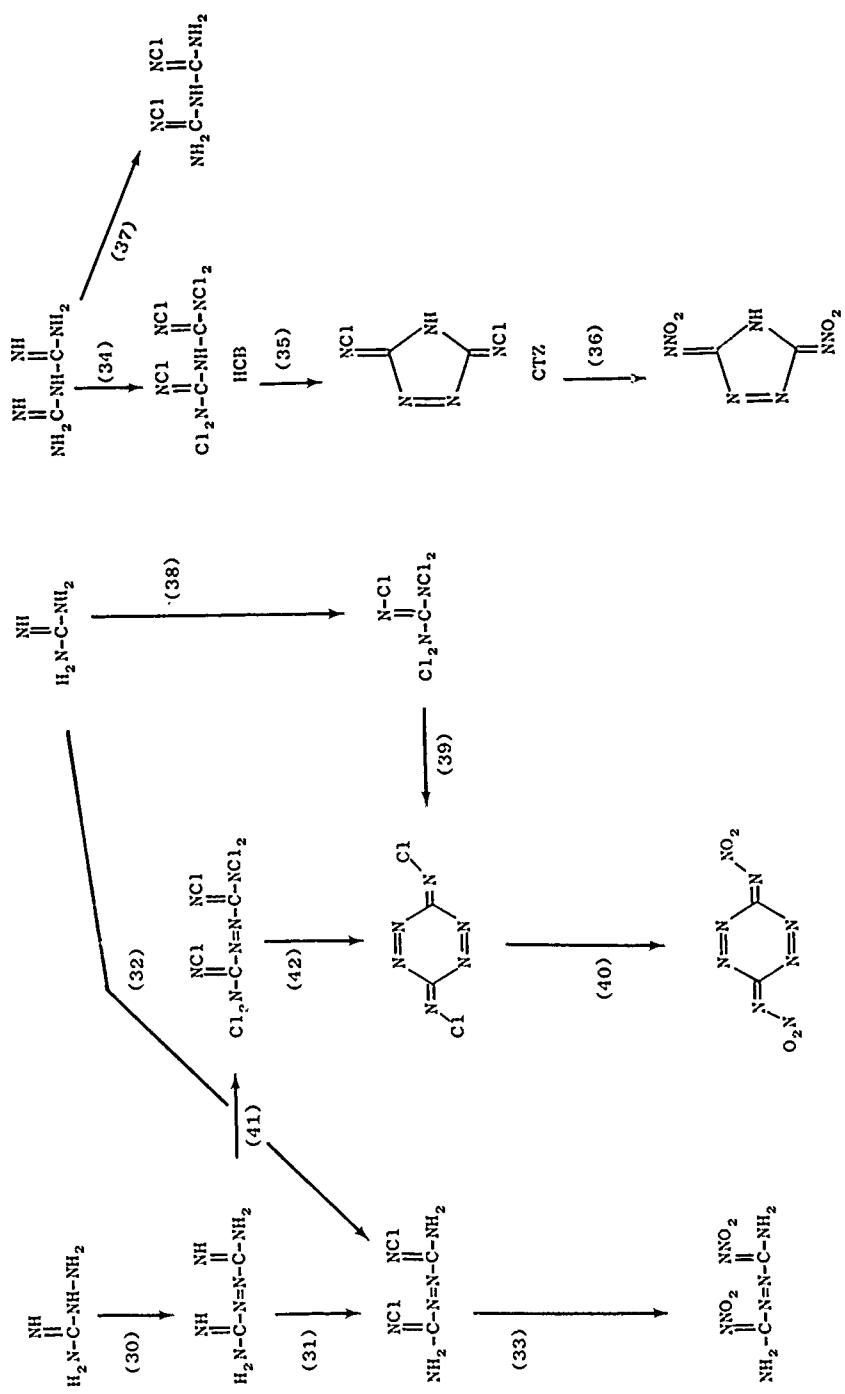
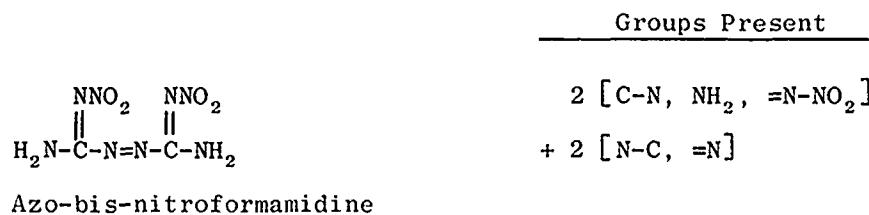


FIGURE 1. PREPARATION OF DINITRIMINO AZO COMPOUNDS

for testing. As an explosive it is balanced to CO and H₂O; its measured density is 1.83 g/cm³.

The density of azo-bis-nitroformamidine was estimated by C. Tarver, who is now working for LLL. Because the densities of similar compounds are not available, data on compounds containing the N-C and =N groups were used, along with the density of nitroguanidine.



Density data on compounds containing the N-C and =N groups gave an average molecular volume of 8.03 cm³/mol. To obtain the value for [C-N, NH₂, =N-NO₂], it was assumed that the structure of nitroguanidine was NH₂C(=N-NO₂)NH₂, and the average value for changing -NH₂ to -N (bonded to carbons) was taken from Table 1, Report 4, as -17.23 cm³/mol. By this method the molar volume for [C-N, NH₂, =N-NO₂] is 49.93 cm³/mol. Thus, the molar volume calculated for azo-bis-nitroformamidine is 115.92 cm³/mol, and the estimated density is 1.76 g/cm³. The fact that this value is low by 3.8% could be attributed to the assumptions made concerning the structure of nitroguanidine. As more derivatives containing the azo-bis-nitrimino groups are synthesized, the molar volume of this group can be determined accurately and better density estimations can be made.

The proposed synthetic route to NTZ, given in Equations (34-36), employs biguanide as starting material. Biguanide can be chlorinated to hexachlorobiguanide (HCB) by treating it with HOCl in acid solution. HCB is a shock-sensitive, orange solid that melts at 65°C and is stable for long periods if protected from atmospheric moisture. HCB can be

cyclized to 3,5-bis(chlorimino)- Δ' -triazoline (CTZ) by treatment with activated charcoal or by treatment with a base followed by careful acidification. CTZ is a slightly shock-sensitive, yellow crystalline solid that melts at 120°C with decomposition. Efforts to convert CTZ to NTZ by reaction conditions used to convert azo-bis-chloroformamidine to azo-bis-nitroformamidine have not been successful. Little or no organic product is recovered from this reaction, indicating that the triazoline ring decomposes during the nitration. Variation in reaction temperature and reaction time and the use of $\text{HNO}_3\text{-CF}_3\text{COOH}$ in place of $\text{HNO}_3\text{-CH}_3\text{COOH}$ should be examined.

We also found that $\text{NH}_2\text{C}(\text{=NCl})\text{NHC}(\text{=NCl})\text{NH}_2$, which has not been reported previously, can be prepared by the reaction of biguanide with HOCl at pH 5, as shown in Equation (37). Although this compound is of no interest in the current program, it has potential as an interesting intermediate for other highly overoxidized explosives.

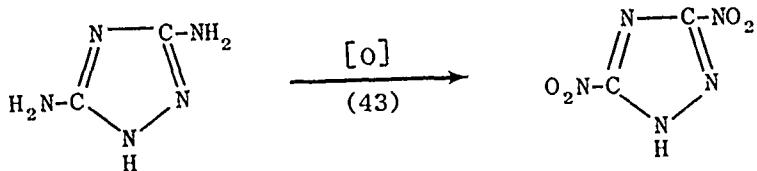
3,6-Bis(nitrimino)-3,6-dihydro-1,2,4,5-tetrazine

Closely related to NTZ is the nonhydrogen compound 3,6-bis(nitrimino)-3,6-dihydro-1,2,4,5-tetrazine, which we attempted to prepare by the reactions shown in Equations (38)-(40). Because Equation (35) involved loss of chlorine and coupling to form an azo group and because we have shown that this is a general reaction for these types of NCl compounds, we felt that pentachloroguanidine could be made to couple twice to form 3,6-bis(chlorimino)-3,6-dihydro-1,2,4,5-tetrazine, as in Equation (39). This reaction was tried several times and gave only low yields of a product insoluble in organic solvents. An elemental analysis of this product indicated an average molecular formula of $\text{CN}_3\text{Cl}_{16}$, which is indicative of a polymeric product. It is evident that the linear coupling reaction is favored over ring formation, even at high dilution, possibly because of the slight strain in the expected tetrazine ring system.

A second possible route to 3,6-bis(nitrimino)-3,6-dihydro-1,2,4,5-tetrazine is shown in Equations (41), (42), and (40). Azo-bisformamidine can be converted to azo-bis(N,N,N'-trichloroformamidine) by reaction with acidic HOCl. Azo-bis(N,N,N'-trichloroformamidine) is an extremely shock-sensitive compound; it forms red-orange plates from hexane that melt at 78-80°C. Conversion of this compound to a tetrazine, as in Equation (42), has not yet been attempted.

Oxidation of Guanazole

One attempt was made to oxidize guanazole to the dinitro derivative shown in Equation (43).



Guanazole (1 g) was slowly added to a mixture of trifluoroacetic anhydride (12.6 ml), 90% hydrogen peroxide (2 ml), and chloroform (18.4 ml) at 5°C. The solution turned from blue-green to yellow over a 90-minute period. Aliquots were taken at 30 and 90 minutes, and the remainder of the material was left to react overnight. After workup, several spots were observed on a silica gel tlc of the crude product. The crude product mixture was run through a silica-gel column with anhydrous acetone. The first cut, a liquid, shows C=O and C-F absorption in the ir, and a sharp singlet at 2.19 ppm and a broad peak at 5.45 ppm in the nmr (integration 3 to 1). This cut appears to contain some trifluoroacetic acid. The remaining three cuts are yellow solids. Their ir spectra show little or no C-O or C-F absorption; however, no C-NO₂

absorption is present either. The nmr spectra show a number of scattered peaks, indicating a mixture of several compounds. None of the materials is sensitive to a sharp hammer blow.

Experimental Details

The following experiments are given in detail because they describe the synthesis of either new compounds or key intermediates. The general descriptions of other reactions studied during this program are given in the preceding discussion. Elemental analyses were performed by Georgina Hum on a Perkin-Elmer Autosampler, infrared spectra were run on a Perkin-Elmer 247 Spectrometer, ¹H nmr spectra were run on a Varian EM-360 spectrometer, and ¹³C and ¹⁹F nmr were run on a Varian XL-100 spectrometer.

3,5-bis(chlorimino)-Δ'-1,2,4-Triazoline

To a solution of 0.75 mol (30 g) sodium hydroxide in 30 ml water cooled to 5°C was added, portionwise over 30 minutes with vigorous stirring, 0.025 mol (7.6 g) hexachlorobiguanide. The deep-orange-colored solution obtained was stirred for another hour at room temperature and then cooled in an ice/salt bath. Concentrated HCl was then added carefully, and a violent evolution of chlorine was observed at pH 6.0, yielding a bright-yellow solution. This solution was extracted six times with 50-ml portions of chloroform, and the combined chloroform solutions dried over MgSO₄ and concentrated on the rotary evaporator at 25°C. The resulting yellow solid was recrystallized from chloroform/hexane, forming pale-yellow needles. Yield 1.1 g (27%). Mp 120°C (dec). Elemental analysis calculated for C₂HN₅Cl₂: C, 14.46; H, 0.60; N, 42.17. Found: C, 14.97; H, 0.57; N, 42.69. IR (CHCl₃): 2.94 μm (m, N-H), 6.04 μm (w, N=N), 6.18 μm (s, C=N), 6.23 μm (w, C-N), and 8.58 μm (s, N-Cl-).

3-Amino-6-hydroxylamino-s-tetrazine

To 18.4 ml chloroform at 0°C was added 12.6 ml trifluoroacetic anhydride over a 15-minute period at 0-5°C. To this mixture was added 2 ml (82 mmol) 90% hydrogen peroxide at 0-5°C with very vigorous

stirring over 20 min. Diaminotetrazine, 1 g (8.9 mmol), was added in small portions to the mixture at 0-5°C over 15 min. The reaction mixture was stirred at 0-10°C for an additional 20 min and then evaporated to dryness. The residue was extracted with warm acetone, filtered, and dried. Elemental analysis calculated for $C_2H_4N_6O$: C, 18.75; H, 3.15; N, 65.60. Found: C, 19.59; H, 3.02; N, 64.76.

Hexachlorobiguanide

To 200 ml 5.2% NaOCl (0.20 mol) over 40 ml CFC_3 was added a solution of 2.00 g biguanide (0.02 mol) and 16.4 ml 37% HCl (0.20 mol) in 50 ml water. The biguanide solution was added over a period of 20 min. A slight temperature rise was noted, and additional CFC_3 was added to replenish the CFC_3 as it boiled off. After addition of the biguanide, the reaction was stirred for about 15 min or until the aqueous phase was nearly transparent. The CFC_3 phase was separated, dried (Na_2SO_4), and the solvent removed under vacuum to give 6.22 g of a yellow viscous liquid. This material was dissolved in a minimum amount of CFC_3 (~ 30 ml) and placed in a -18°C freezer for several days. The yellow crystalline solid that formed was collected. Yield 2.61 g. Mp 69°C. This compound is very shock sensitive and can be detonated with a light hammer blow. It was identified as hexachlorobiguanide by its elemental analysis. Elemental analysis calculated for $C_2HN_5Cl_6$: C, 7.81; H, 0.34; N, 22.77; Cl, 69.08. Found: C, 8.38; H, 0.34; N, 22.53; Cl, 68.71.

5,5'-Dinitro-3,3'-bi-2-isoxazoline

A solution of 8.11 g (95 mmol) 2-fluoro-2,2-dinitroacetaldoxime¹⁰ in 150 ml methylene chloride was cooled to 0°C, and nitric oxide was bubbled in slowly at 0-5°C until a total of 11 g had been added. The reaction mixture was then allowed to stand at 5°C for 15 hr.

Nitroethylene, 30.5 g (486 mmol), was added to the reaction mixture, and the mixture was refluxed for 16 hr until the evolution of oxides of nitrogen had ceased. The solvent was then evaporated, and the residue was passed through a silica gel column. Initially the eluant was 20% methylene chloride in hexane, but this was increased incrementally until 100% methylene chloride was being used. The fractions eluted with 100% methylene chloride were combined and evaporated to a solid residue, which was recrystallized from ethyl acetate and chloroform, giving white needles that melted with decomposition at 145°C. Yield 2.6 g.

Elemental analysis calculated for $C_6H_6N_4O_6$: C, 31.31; H, 2.63; N, 24.35. Found: C, 31.60; 2.58; N, 24.80. Pmr (CD_3CN): 3.90 ($-\text{CH}_2-$, doublet, area 2), 6.35 δ ($-\text{CH}-\text{NO}_2$, triplet, area 1) (see Figure 2). Cmr (CD_3CN) off resonance, referenced to TMS; 42 (CH_2 , triplet), 106 ($-\text{CH}-\text{NO}_2$, doublet), 152 ppm (C=N, singlet) (see Figure 3). The mass spectrum is shown in Figure 4.

Hexachloroazobisformamidine

To 170 ml 5.25% NaOCl (120 mmol) over 40 ml methylene chloride was added a solution of 1.20 g azobisformamidine dinitrate^{17, 18} (5 mmol) and 11.8 g 37% HCl (120 mmol) in 25 ml water. During the addition, which took 12 min, the mixture was stirred slowly and the temperature was kept at 25-20°C with a cold water bath. After the addition the mixture was stirred until the aqueous phase became nearly clear. The methylene chloride phase was separated, dried ($MgSO_4$), and the solvent removed, leaving 0.32 g of a dark-orange liquid that crystallized after sitting for 16 hr at 5°C. This material was recrystallized from hexane/dichloroethylene to give a crystalline product that melted at 74-76°C (dec.). This product was very sensitive and could be detonated with a light hammer blow. It was identified as hexachloroazobisformamidine by its infrared spectrum.

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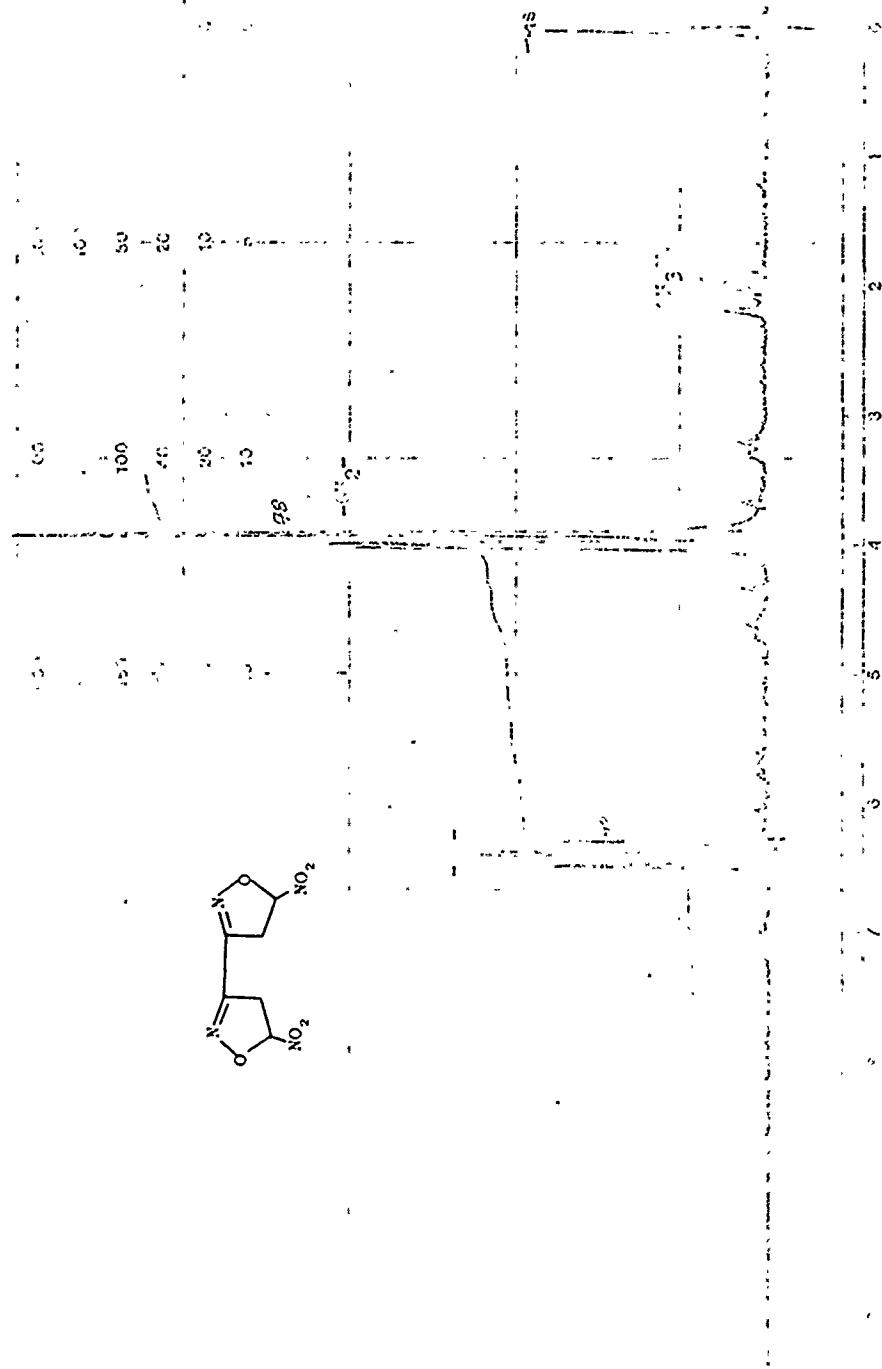


FIGURE 2. ^1H NMR SPECTRUM OF 5,5-DINITRO-3,3'-BI-2-ISOXAZOLINE

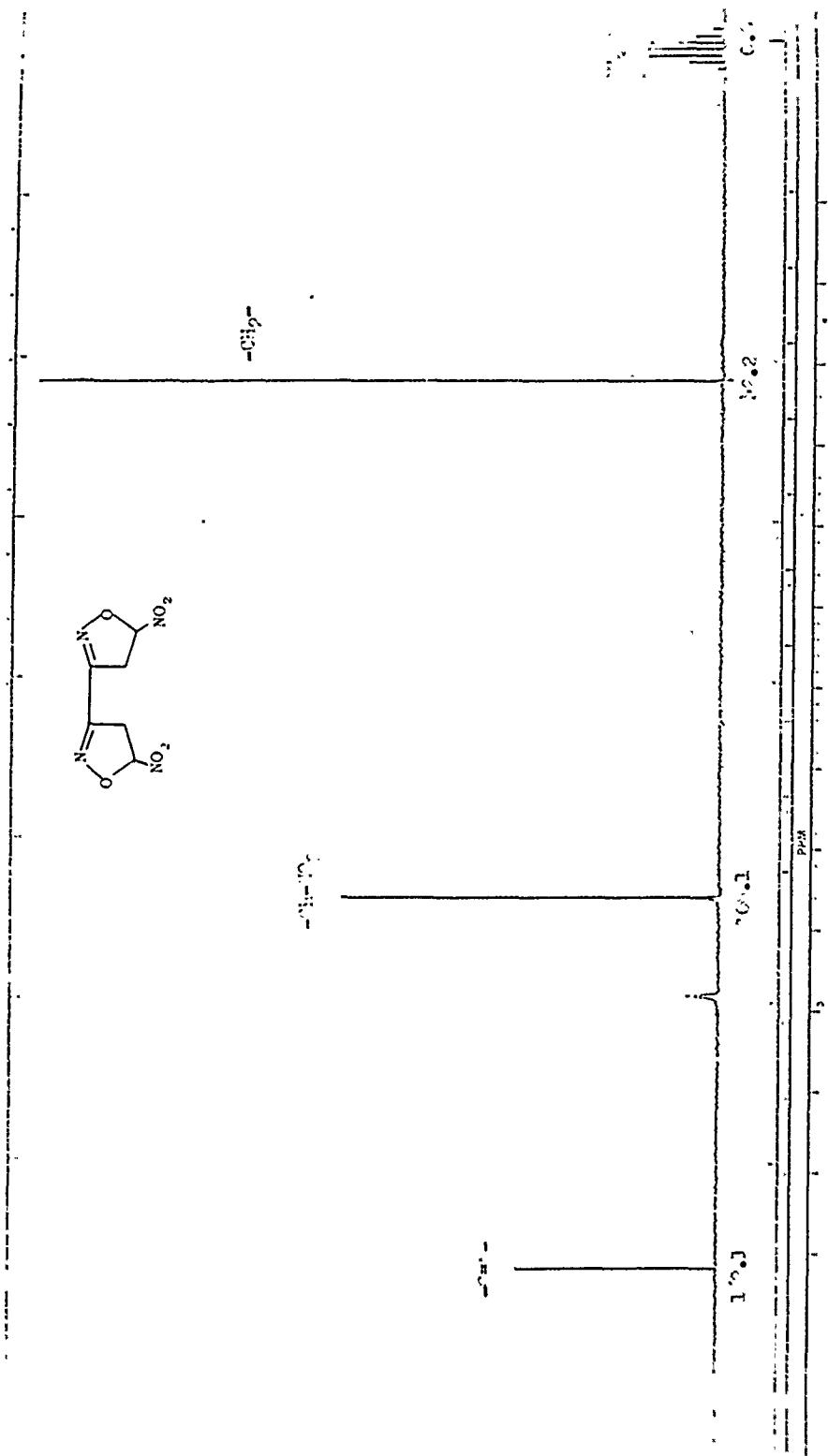


FIGURE 3. ^{13}C NMR SPECTRUM OF 5,5'-DINITRO-3,3'-BIS-2-ISOXAZOLINE

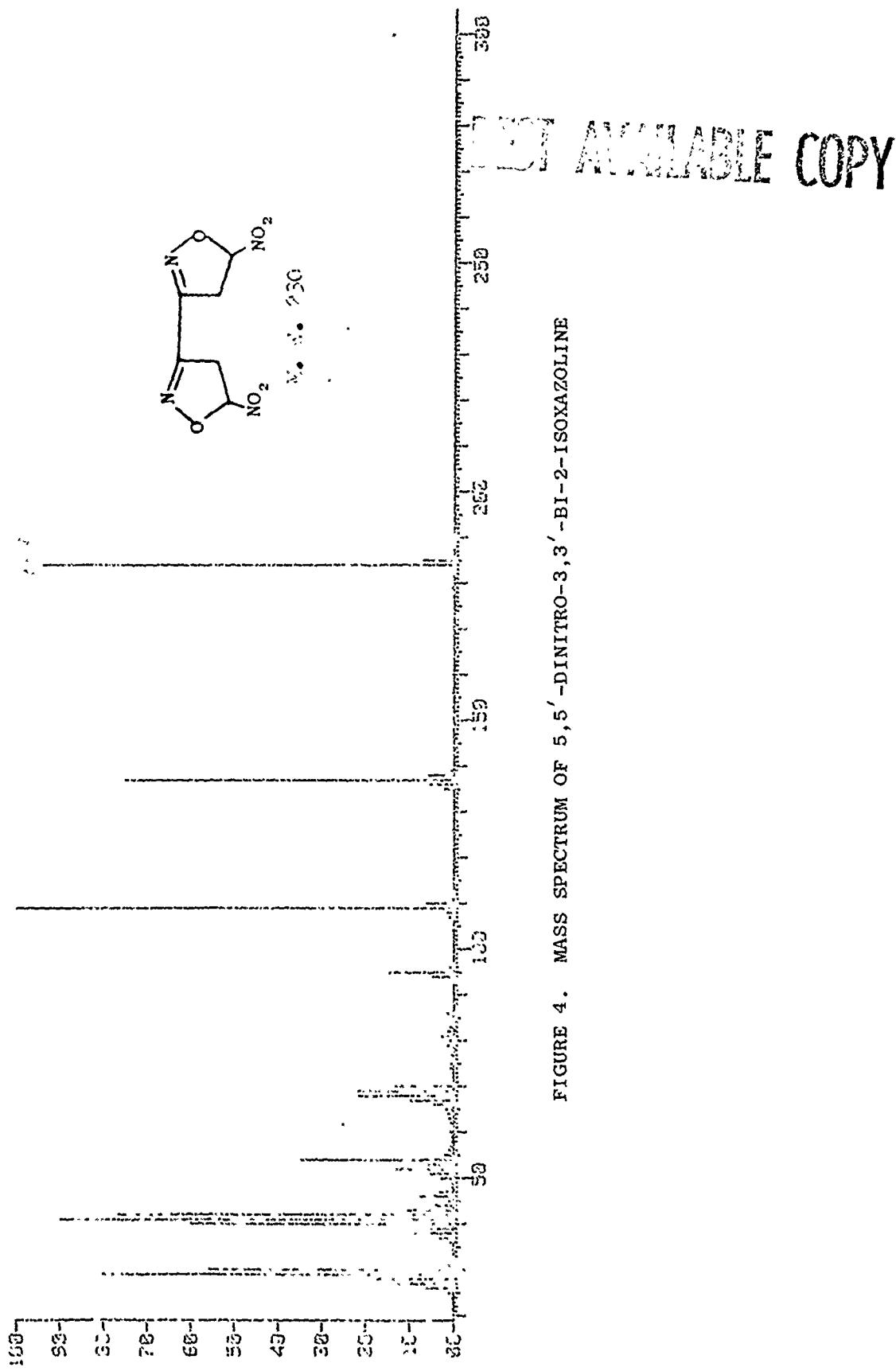


FIGURE 4. MASS SPECTRUM OF 5,5'-DINITRO-3,3'-BI-2-ISOXAZOLINE

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19. KEY WORDS (Continued)

20 ABSTRACT (Continued)

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and 9.0% were more than 4% different from the measured densities. Thus, of the densities estimated in this study, 82% were within 3% of the measured density. The average absolute error in density was approximately 0.022 g/cm³, and the absolute error in density exceeded 0.04 g/cm³ for only 24 of the 168 compounds (14.3%). The largest errors occurred for compounds with several bulky, highly polar groups in close proximity, and for compounds containing groups whose calculated molar volumes were based on density data for only two or three compounds. As more density data for a certain group configuration become available, the molar volume can be determined more accurately, and the overall agreement between measured and estimated densities of compounds containing that group should improve.

Synthetic work was carried out on a number of newly postulated explosives or explosives whose syntheses were expected to be difficult. Progress was made toward the synthesis of 3,6-bis(nitrimino)-3,6-dihydro-1,2,4,5-tetrazine and 3,5-bis(nitrimino)-Δ'-1,2,4-triazoline, which contain no hydrogen and are highly energetic. Syntheses were developed for the preparation of the important intermediates hexachloroazobisformamidine and 3,5-bis(chlorimino)-Δ'-1,2,4-triazoline. In addition, the oxidation of diaminotetrazine was partially successful in that the partially oxidized intermediate, 3-amino-6-hydroxylamino-s-tetrazine, was isolated.

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